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Use of Accelerated Calcite Precipitation Method to Investigate Calcium Carbonate Precipitation from Recycled Concrete for Drainage System Applications

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USE OF ACCELERATED CALCITE PRECIPITATION METHOD TO
INVESTIGATE CALCIUM CARBONATE PRECIPITATION FROM
RECYCLED CONCRETE FOR DRAINAGE SYSTEM APPLICATIONS

by

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for the degree of Doctor of Philosophy
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ABSTRACT

Recycled concrete aggregate (RCA) is a sustainable construction material that is a viable option for use in drainage systems by replacing virgin aggregate. Replacing virgin aggregate with RCA is beneficial from both economic and environmental perspectives. However, the use of RCA as pipe backfill materials may cause a long-term performance issue such as potential clogging due to fines accumulation and calcite precipitation on filter fabric. Previous studies investigated the long-term performance of RCA regarding flow rate. Therefore, this study investigated calcite precipitation potential of RCA. The Accelerated Calcite Precipitation (ACP) procedure was devised and used to estimate “life-time” calcite precipitation of RCA for French Drains. The ACP procedure was studied further and improved to optimize the calcite precipitation procedure. The enhanced method was used to compare the calcite precipitation of limestone and RCA samples - sources with varying chemistry and history. Key findings are (1) the clogging due to calcite precipitation of RCA is not as significant as clogging due to the existing and/or accumulated fines, (2) the calcite precipitation can be increased with a temperature of 75°C and 17-hour heating time, and (3) the potential for calcite precipitation from RCA is not as significant as limestone for Type I underdrain gradation.

Dedicated to

***My husband, Justin
My parents, George and Audrey
And my sister, Dana***

Your support and encouragement kept me going when I didn't think I could make it.

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CHAPTER ONE: INTRODUCTION

Recycled Concrete Aggregate (RCA) can be defined as a material that consists of about 60 to 75 percent high quality, well-graded aggregates bonded by a hardened cement paste. RCA can be obtained from obsolete concrete structures including, buildings, roads, or runways. Other structures such as Portland cement concrete curbing, sidewalks and driveways which are typically reinforced and should go through a screening process which uses magnetic separators to extract the ferrous material. Some reinforcement such as welded mesh, however, are much more difficult to separate, in such cases the final RCA product may contain some metal debris. For example, the concrete waste shown in Figure 1 was demolished during a project at Patrick Air Force Base in Florida and hauled to a facility. In Brevard County, Florida, material such as this can go to two different types of facilities, (1) a landfill such as the Central Disposal Facility in Cocoa, Florida, or (2) a concrete waste recycling company such as Space Coast Crushers in Rockledge, Florida. The recycling facility will crush the concrete waste into small aggregate and sell it to be re-used as base material, usually in pavement applications.



Figure 1: Hauling of concrete waste on Patrick Air Force Base, Florida

Problem Statement

RCA is limited by specifications for potential use in drainage applications. The Florida Department of Transportation (FDOT) specifications for coarse aggregate stipulates that aggregate can be composed of reclaimed Portland cement concrete (PCC) such as the concrete waste in Figure 1 if it meets the stated gradation, Los Angeles (LA) abrasion, source and contamination requirements. The use of reclaimed PCC for coarse aggregate is limited to pipe backfill under wet conditions, underdrain aggregate and bituminous

mixtures. The FDOT specification for fine aggregate does not include any mention of the use of reclaimed PCC.

The specifications pertaining to reclaimed PCC for use in coarse aggregate does not include applications for French drain systems. French drains are used to redirect water from the ground surface to subsurface pipes. Filter fabric and aggregate are used to filter the water as it flows through the drain. The fines in reclaimed PCC and the potential for calcite precipitation introduce the risk of clogging French drain systems, which would reduce their performance.

In addition to French drains, type I underdrains have not been addressed by the FDOT specifications. Underdrain systems are used to collect and redirect subsurface water such as groundwater, so that it does not rise to the surface and saturate the road base. The water enters through the filter fabric, flows through the aggregate and into the perforated pipe. Type I underdrains are designed to include only fine aggregate that meets the specifications in Section 902. The risk of using reclaimed PCC is its clogging potential due to calcite precipitation.

Research Objectives

This study investigates the potential for clogging of recycled (reclaimed) concrete as aggregate in drainage applications. Previous work on the French drain application will be studied and compared with current work on the Type I Underdrain application. Factors

affecting the performance of RCA in French drain systems include the effects of fines and hydraulic gradient on permeability and the potential for calcite precipitation. The potential for calcite precipitation from recycled concrete in type I underdrains is also investigated in this study. The results for recycled concrete are compared to the calcite precipitation from limestone. Limestone is an abundant natural aggregate in Florida.

Research Methodology

The Accelerated Calcite Precipitation (ACP) procedure was used to investigate the potential for calcite precipitation. This method was used for the French drain application, and then investigated to optimize the precipitation in each cycle by varying the heating temperature and heating time. The enhanced ACP method was then used to compare the calcite precipitation for recycled concrete and limestone samples. These results were then compared to the results of the original ACP method. Permeability testing was also used to investigate the clogging potential for recycled concrete in French drain applications.

Organization of Dissertation

The dissertation is organized as follows.

Chapter Two provides background information on calcium carbonate and its three polymorphs, limestone, RCA and calcite precipitation in nature.

Chapter Three includes the previous investigation of the clogging potential of RCA in French drain systems using the prototype ACP test method.

In Chapter Four, the ACP procedure is enhanced by exploring the effect of heating temperature and heating time on the calcite precipitation reaction.

In Chapter Five, the enhanced ACP procedure from Chapter Four was used to study and compare the calcite precipitation of RCA and limestone samples. These samples were from different sources and graded to meet the specifications for type I underdrains.

Chapter Six presents the summary and conclusions from the study.

CHAPTER TWO: LITERATURE REVIEW¹

Calcium Carbonate Polymorphs

Calcium carbonate exists in three polymorphs: (i) calcite, (ii) aragonite, and (iii) vaterite. Figure 2. Calcite has a rhombohedral structure while aragonite has an orthorhombic structure (Bragg, 1924; Caspi, et al., 2005; Oates, 1998). Vaterite is not limited to a single lattice structure, but more of a hybrid of at least two crystal lattice systems (Demichelis, et al., 2013; Kabalah-Amitai, et al., 2013). Another prevalent form of calcium carbonate is dolomite, which contains magnesium. Like calcite, dolomite has a trigonal rhombohedral structure (Oates, 1998).

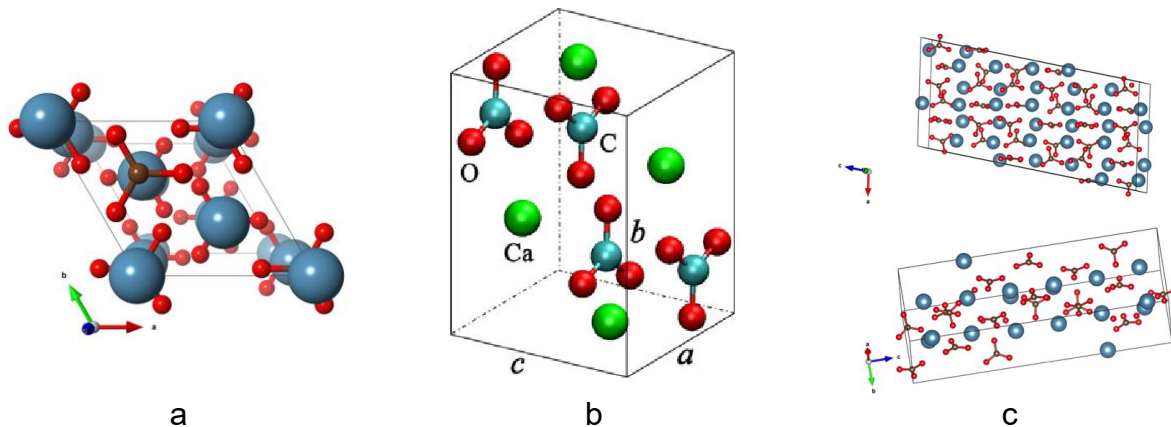


Figure 2: Unit cell of calcium carbonate polymorphs (a) calcite, (b) aragonite (Zhang & Chen, 2013) and (c) vaterite (Demichelis, et al., 2013)

The most thermodynamically stable polymorph of calcium carbonate is calcite, which is found in geological sources such as limestone rocks. Aragonite is not as stable as calcite

¹ This chapter includes previously published content.

McCulloch, T., Kang, D., Shamet, R., Lee, S.J., Nam, B.H. (2017). "Long Term Performance of Recycled Concrete Aggregate for Subsurface Drainage." *Journal of Performance of Constructed Facilities*, 31 (4), 4017015

but can also be found in nature (Oates, 1998; Boynton, 1980; Caspi, et al., 2005). Vaterite is the least stable and not as naturally abundant as calcite and aragonite but can be detected in biominerals such as shells (Kabalash-Amitai, et al., 2013; Gopi, et al., 2013). These polymorphs of calcium carbonate have been studied for many years.

Seigel and Reams (1966) studied precipitates from natural and artificial calcium carbonate sources. Each sample was washed with and submerged in distilled water before having CO₂ bubbled in the solution for 20 minutes. The leachate was filtered and divided into two halves, of which one half was exposed to another round of CO₂ bubbling. Both halves were placed in a drying oven or refrigerator. Their results showed that calcite was the predominant precipitate at lower temperatures (< 50°C) while aragonite was dominant at higher temperatures (> 50°C). There was no difference in the precipitate for the natural samples that were bubbled once or twice, but artificial samples showed a higher concentration of aragonite in samples that were bubbled once (Siegel & Reams, 1966).

Classification of Limestones

Limestone can be categorized based on the magnesium content. Boynton (1980) categorized pure limestones as high calcium when they are 100% calcium carbonate, and dolomitic with 45.7% magnesium carbonate and 54.3% calcium carbonate. Most limestones have 1 – 3% impurities, which means that high calcium limestones are realistically 97 – 99% calcium carbonate and dolomitic limestones are 40 – 43% dolomite

(Boynton, 1980). Oates (1998) classified limestones like Boynton, but with more classes. These classes, based on the concentration and type of carbonate, are summarized in Table 1.

The physical properties of limestone are summarized in Table 2. The specific gravity ranges between 2.71 and 2.86, depending on the dominant calcium carbonate polymorph in the limestone. Absorption rates can range from 0.4% to 20% depending on whether the limestone is dense or chalky (Oates, 1998). Limestones that are used as aggregate would likely be closer to the dense side of the range (~0.4%). Kahraman (2007) recorded an LA abrasion loss of 28.9% while Behra et al (2014) noted that limestones have a 7% -9% lower saturated surface dry (SSD) density than RCA.

Table 1: Classification of limestones (Oates, 1998)

Class	Carbonate Concentration	Type of Carbonate
Ultra high calcium	> 97%	Calcium carbonate
High calcium/ chemical grade	> 95%	Calcium carbonate
High purity carbonate	> 95%	Calcium and magnesium carbonate
Calcitic	< 5%	Magnesium carbonate
Magnesian	5 – 20%	Magnesium carbonate
Dolomitic	20 – 40%	Magnesium carbonate
High magnesium	40 – 46%	Magnesium carbonate

Table 2 : Physical properties of limestone

Specific Gravity	Absorption	LA Abrasion	^a SSD	Reference
		28.9%		(Kahraman, 2007)
	200% – 300% < RCA		7%-9% < RCA	(Behra, et al., 2014)
2.72-2.86 g/cm ³	0.4% - 20%			(Oates, 1998)
2.7102				(Boynton, 1980)

^a SSD: Saturated Surface Dry

RCA Production, Uses and Properties

Recycled concrete is repurposed as aggregate from construction and demolition waste. The recycling facility evaluates, sorts, crushes, sieves and washes the concrete. Contaminants are also removed in the process (Verian, et al., 2018; Behera, et al., 2014; de Brito, et al., 2016). Once the concrete waste has been processed by the facility, it can be sold for various applications.

RCA can be used to replace natural aggregate in asphalt concrete applications (Brasileiro, et al., 2016), in subsoil application (Mikulica & Hela, 2018), in pavement subbase applications (Silva, et al., 2014), concrete production (Meddah, 2017; Silva, et al., 2014; Verian, et al., 2018; Behera, et al., 2014; de Brito, et al., 2016), as well as drainage applications (Behring, 2013; Behring, et al., 2014; Nam, et al., 2015).

Recycled aggregate concrete is concrete that has been produced with recycled aggregate, usually RCA. The performance of recycled aggregate concrete depends on

the quality of the recycled aggregate which is defined by its properties (de Brito, et al., 2016; Behera, et al., 2014; Meddah, 2017; Silva, et al., 2014). Silva et al (2014) developed a classification system for recycled aggregates. The values in Table 3 represent the ranges for class A RCA for which RCA has the highest probability (Silva, et al., 2014). Typical RCA properties are summarized in Table 3. Some of these RCA properties differ from the typical ranges found in natural aggregate. For example, the SSD for RCA is 7% - 9% lower than natural aggregate and the water absorption is 2 - 3 times higher than natural aggregate (Behera, et al., 2014).

Table 3: RCA properties

Specific Gravity	Absorption	LA Abrasion	^a SSD	^b ODD	Reference
1.91 – 2.70	0.5% - 14.75%	20% - 51.5%			(Verian, et al., 2018)
	4.57 – 4.66	11.5 – 12.2	2475 - 2481	2367 - 2370	(de Brito, et al., 2016)
	1.5% – 3.5%	40%		< 2600	(Silva, et al., 2014)

^a SSD: Saturated Surface Dry

^b ODD: Oven Dried Density

RCA can be used in construction as a substitute for virgin aggregate. The reuse of construction demolition waste has received attention for its environmental and economic benefits as it reduces waste disposal cost and contributes to the conservation of natural resources (Ann, et al., 2008; Poon, et al., 2004; Zaharieva, et al., 2003; Hendricks & Pietersen, 2000). RCA consists of approximately 65% to 70% aggregate and 30% to 35% cement paste, by volume (Poon, et al., 2004). Studies show that the cement paste in RCA

affects its performance as a higher content increases the porosity, absorption and lower abrasion resistance (de Juan & Gutierrez, 2009; Shayan & Xu, 2003; Nagataki, et al., 2000; Vancura, et al., 2010).

The use of RCA as a road pavement base and subbase layers has been the topic of study for researchers who have concluded that RCA shows poor permeability characteristics (Song, et al., 2011; Bennert & Maher, 2008; Paige-Green, 2010). Other studies show that the clogging can be caused by recementation and the accumulation of calcite precipitation (Song, et al., 2011; Snyder, 1995; Meuthel, 1989; Tamirisa, 1993). The study that was performed by MnDOT found that 17 to 84% permittivity loss in geotextile filter fabric over 8 years was a result of calcite precipitation while the remaining loss was a result of non-carbonate material (RCA fines) (Snyder & Bruinsma, 1996). Another study on the Lakeville test beds in 1989 showed that after 3 years, 70% of the loss of permittivity in filter fabric was due to calcite while the remaining 30% was due to non-carbonate material (Bruinsma, et al., 1997).

Recently, the use of RCA as pipe backfill materials in exfiltration trench system has been studied from the short-term performance perspective. Previous studies have investigated chemical and physical properties and behaviors of RCA as well as the permeability performance of RCA (Behring, et al., 2014; Behring, et al., 2014; Behring, et al., 2014; Behring, et al., 2015; Kim, et al., 2014; Nam, et al., 2014; Nam, et al., 2015; Nam, et al., 2016; Nam & An, 2016). Kim et al. (2014) reported that RCA stored outside over long

periods of time may not produce the significant level of recementation that causes clogging of flow. Nam et al (2015) conducted a nationwide survey of state agencies and reported that RCA is mainly used in road base/subbase not in exfiltration trench due to clogging potential.

Survey on RCA Use Within the USA

A survey was conducted in 2013 to determine whether state Departments of Transportation (DOTs) used RCA for exfiltration trench applications. The responses to the following survey questions are shown in Table 4.

Q1. Does your state DOT use reclaimed concrete aggregates (RCA) in exfiltration trench?

Q2. Does your state DOT have a specification for the RCA used in exfiltration trench?

Q3. Has your state DOT experienced any problem (i.e. poor drainage performance, environmental issue, etc.) by using the RCA in drainage systems?

None of the state DOTs that responded said they used RCA specifically for drainage applications. Some states had issues with using RCA for drainage applications. New Jersey DOT was concerned about the pH of water flowing through the RCA as well as its fines content which is at least 10%. Indiana DOT has used RCA as pavement subbase material, but experienced clogging of the X drain system due to high fines content and possible cement hydration. Ohio DOT does not allow aggregate in underdrain applications due to previous issues with environmental pH runoff and re-cementation. They have also experienced tufa development due to RCA reaction with the roadway runoff. Kentucky DOT does not allow RCA for drainage applications due to an experience where the outwash clogged screens and killed vegetation.

Table 4: Responses to Survey Questions

State DOT	Q1	Q2	Q3	Note
Alabama	No	Not specifically	N/A	We do allow reclaimed concrete aggregates in embankments and as base material after rubblization but have not seen a request for use as a drainage medium.
Arizona	No	No	No	
Connecticut	No	No	No	
Georgia	No	No	No	
Indiana	No	No	Yes, but not in this specific application	We have used RCA as a subbase material beneath concrete pavement and experienced clogging of the X drain system. This was due to the much higher percentage of minus #200 sieve material in the RCA than we have in virgin aggregate and possibly un-hydrated cement in the RCA. Also, we have had leachate issues in other applications. We currently allow RCA in subgrade treatments and have a research project ongoing to study using RCA in concrete at varying percentages.
Kentucky	No	No	N/A	Never approved for drainage application. RCA is not an approved material in Kentucky but I have attached old special note for your information. The only time I know of it being used the outwash clogged screens and killed vegetation. Pictures are attached. Other concerns would be clogging of fabric and corrosion of metal pipes (see the photos below).

Louisiana	No	No	N/A	
Maine	No	No	N/A	
Mississippi				Mississippi DOT uses and/or allows crushed concrete as a substitute for crushed stone base and as a substitute for granular material used on shoulders.
Montana	No	No	N/A	
Nebraska			N/A	We allow use of crushed concrete, bituminous millings, or aggregate D (sand and gravel mix) in our typical 4" foundation course below PCC pavements. We require the use of crushed gravel or crushed rock for our granular subdrains (French drains). We typically do not wrap our granular drains with fabric unless we are also installing perforated pipe longitudinal drains. See attached special provision for granular subdrain gradation and detail.
Nevada	No	No		We use drain rock.
New Hampshire	No	No	No	
New Jersey	No	No	No	In NJ, we have concerns regarding the pH of water flowing through RCA so we have not used it in drainage systems. Most of the RCA that we have also has a high percentage of fines - 10% or more. This material is pretty much impermeable. A different gradation of RCA may be drainable but we don't have anyone who wants to make a different gradation.
New York State	Not yet	Not yet	N/A	Current NYSDOT specifications do not allow RCA as a drainage filter

				<p>material. This is something that we plan to change in the future.</p> <p>We allow RCA as embankment, as subbase gravel, and as select fill at this time.</p> <p>We do use RCA in a large number of other applications and have had no specific concerns.</p>
North Dakota	No	No	N/A	We have used it as a drainable base layer (cement stabilized) without any problems.
Ohio	No	No	No	<p>Currently ODOT does not have formal established specifications for exfiltration trenches as they are still experimental in use in Ohio. Our latest testing uses natural sands with a cement or asphalt treated free draining system at the top.</p> <p>Your applications may not be quite the same. For pavement drainage we use 4 or 6 inch underdrains allowing only #8, #89 or #9 ACBF aggregate, gravel or limestone. We require the underdrain excavation to be filterfabric lined. We do not allow RCA in this application.</p> <p>OHIO has had problems with RCA environmental pH runoff and re-cementing of the product causing us pavement problems. Due to that we don't allow the use of RCA as aggregate roadbase. We have had tufa development in pavement drainage systems because of RCA used for undercuts for repair of poor</p>

				pavement subbase. We also had laboratory research looking at RCA as a roadbase material that predicted tufa due to reaction between RCA and roadway runoff into the drainage.
Oklahoma		No	No	Our specifications do not specifically address the use of RCA in this application. Technically it could be used if it met the specifications. To our knowledge RCA has not been used in this application.
Ontario (Canada)	No	No	N/A	We use reclaimed concrete aggregate only in granular base/subbase
Rhode Island	No	No	N/A	RIDOT does not use recycled concrete solely on its own. It could be blended to create a processed borrow material.
South Carolina	No	No	N/A	
Texas	No	No	No	Our specifications do not prevent the use of RCA, but there are no know uses of RCA for this purpose. The specifications are written that would indirectly discourage use of RCA.
Utah	No	No	N/A	Our standard specification, 02056 Embankment, Borrow, and Backfill, under Section 2.1.A. states: Provide materials free of contamination from chemical or petroleum products for embankment and backfill placements. Materials may include recycled Portland cement concrete. Do not include asphalt pavement materials. So, you can see the material is allowed but it must meet the

				same specification as virgin materials. I have attached a copy of this specification for your information. We do not have a separate specification for French Drains, Exfiltration trench or RCA.
Washington	No	N/A	N/A	We have used RCA for base and subbase effectively and have a study underway to look at using it back in PCC.

Potential Problems of RCA as Drainage Materials

Rehydration

Recycled concrete typically contains a small portion of unhydrated cement because the original concrete did not fully hydrate during the initial process. There may be a risk for significant quantities of RCA fines containing unhydrated cement to experience cementation when exposed to water molecules. The risk is minimized by eliminating fines when RCA is used in drainage foundation layers. The Minnesota Department of Transportation (MnDOT) has experienced that one year of exposure to the elements did not rehydrate stockpiled coarse and open-graded materials and do not expect any rehydration of these materials in the long term due to particle surface for coarse particle binding (Snyder, 1995).

Katz (2003) studied the properties of concrete that was made with recycled aggregate from partially hydrated concrete. The effects of using partially hydrated concrete as aggregate in the new concrete were investigated along with the properties of the new

concrete that was made with the partially hydrated concrete. The aggregate samples were produced by crushing 1, 2 and 28 day old concrete to coarse, medium and fine gradation and oven drying to avoid additional hydration. Exposed hydrated and unhydrated cement was significantly higher for the fine gradation during the crushing process. The study determined that high cement paste content contributes to high porosity in the recycled aggregate, absorption was higher with recycled concrete, and the cement paste that adhered to the natural aggregates was constant for each gradation, despite the crushing age. The new concrete that was made with 1 day old RCA resulted in better properties than the other samples. The cementing potential of recycled aggregates decreased to no potential after 3 days. Recycled aggregates that were made from 1 day old concrete had more cementing potential than aggregates made with 28 day old concrete, which had none, and proved to be weaker (Katz, 2003).

Clogging in Drains

Geotextile filter fabric clogging can be caused by different means which include RCA fines and calcite precipitation. A study by the Iowa DOT (Steffes, 1999) showed that calcite deposits had grown on the drain outlet wire mesh rodent guard to the extent of complete clogging for some cases (Figure 3).



Figure 3: Clogging in drain outlet wire mesh rodent guard due to calcite precipitation (Steffes, 1999)

Snyder and Bruinsma (1996) summarized a study by the MnDOT which has experience with geotextile filter fabric and RCA. Filter fabric samples were obtained in 1989 and 1993 from project locations to be tested for permittivity loss. An average of 50% and 53% permittivity was lost in 4 and 8 years, respectively. The greatest loss in permittivity was observed on the sidewall samples while less permittivity loss was observed in samples from the top and bottom of the pipe. Calcite precipitation was determined to be responsible for 17-84% of the permittivity loss, with the remaining loss coming from non-carbonate material. Each sample was soaked in acid which reacted with the calcite to measure the calcite buildup, which means that the leftover material was non-carbonate in nature (Snyder & Bruinsma, 1996).

Bruinsima et al (1997) presented the 1989 MnDOT study of Lakeville test beds which were constructed with a 0.015 ft/ft slope drain to move rainwater to an edge drain system and contained RCA and virgin aggregate. The recycled fines in the test beds with RCA caused a higher pH value than the beds with virgin aggregate. Filter fabric samples were taken from the top and bottom of the wrapped edge of the drains after 3 years to test the permittivity. Results showed that although samples from test beds with virgin aggregate and RCA had permittivity loss, the losses in the samples from the RCA test beds were due to calcite precipitation. In fact, approximately 70% of the permittivity loss was attributed to calcite precipitation while the remaining 30% was attributed to non-carbonate material (Bruinsma, et al., 1997).

RCA Field Studies

Truck Highway 212

Edge drains near Glencoe, MN were retrofitted in 1985 along Truck Highway (TH) 212. The existing base which included natural aggregate at the dense-graded aggregate classification. Samples were obtained from the longitudinal edge drain wrap after four years in service for permittivity testing. The samples taken from the top of the pipe had an average permittivity loss of 1.0/sec whereas the samples from the bottom of the pipe had an average permittivity loss of 0.5/sec. The permittivity loss from the top of the pipe fell below the MnDOT Specification 3733 limit of 0.7/sec. The losses in the pipes were attributed to buildup of non-carbonated material which proves that significant reductions in permittivity is not unique to applications with recycled concrete materials. Studies of

permittivity loss related to recycled concrete aggregate should include the contribution of non-carbonate materials (Snyder, 1995).

Truck Highway 15

Snyder (1995) also reviewed a MnDOT study in which eight 400-ft by 27-ft test sections were constructed with edge drains on both sides of the pavement. Three of these sections used RCA in the pavement foundation while the remaining five sections did not use RCA (Snyder, 1995). Muethel (1989) demonstrated that the precipitation yield from this study was higher than that of the Lakeville study (Meuthel, 1989). The difference in the results were due to variations in water flow patterns as well as wetting and drying conditions at the sites. Study results show that RCA in untreated pavement bases may have more of a negative impact on drainage outflow than natural aggregates. The risk of the impact can be minimized by using open-graded materials or unwrapped drainage pipes, or by blending RCA with natural crushed rock. Greater outflows are achieved by RCA in open-graded bases with unwrapped pipes than the natural base in a wrapped pipe section.

Permeability Study for French Drain Gradation

The objective of this study was to evaluate the long-term performance of RCA for use in subsurface systems (McCulloch, et al., 2017). A long-term permeability test was used to investigate the drainage performance of RCA with geotextile fabric.

RCA obtained from a construction and demolition (C&D) waste recycling facility in Orlando, Florida was ground to fines and tested using standard procedures as shown in

Table 5. These tests show that the RCA sample had a low specific gravity, and high absorption capacity, relative to natural aggregate. A sieve analysis test was also conducted on three RCA samples of different masses with 10, 15, and 20 kg. The particle size distributions shown in Figure 4 illustrates that the RCA samples do not comply with the ASTM D448-12 standard for grading. In order to comply with No. 4 gradation specification, the “as is” RCA specimens were recombined with smaller fractions. Thus, the RCA, used in the permeability tests, fell within the maximum and minimum gradation limits for subsurface drainage aggregate size as defined by FDOT standards.

Table 5: Physical properties of RCA sample

Property	Test Value	Test Method
Specific gravity (oven dry)	2.16	ASTM C127
Absorption capacity (%)	6.4	ASTM C127
Bulk density (oven dry, kg.m ³)	1210	ASTM C29
Void content (%)	43	ASTM C29
LA abrasion mass loss (%)	44	ASTM C535

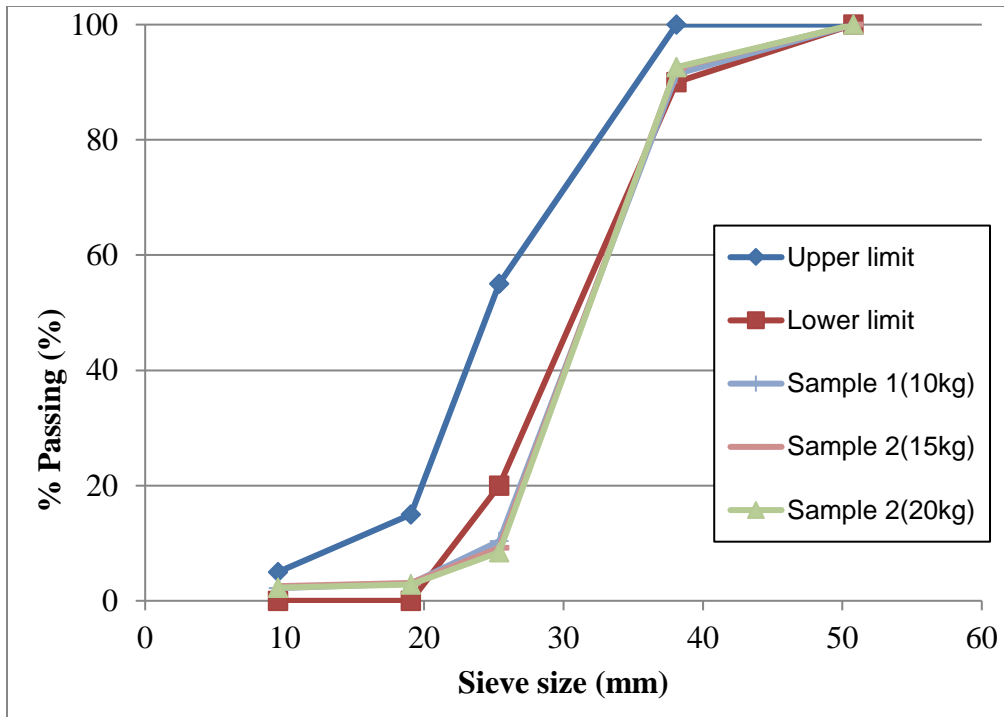


Figure 4: Sieve analysis data for RCA samples.

Filter fabric, or geotextile, is used in actual construction of subsurface drains to restrict movement of the aggregate into the surrounding natural soil, and soil into the drainage aggregate. The governing property of geotextiles, which is most important in subsurface drainage applications, is the apparent opening size (AOS). Depending on the percent of fines (passing the No. 200 sieve) the AOS required for French Drains vary from No. 40 to No. 70 sizes. Since the percent of fines for the No. 4 gradation is less than 15%, a geotextile of AOS equivalent to the No. 40 sieve (0.0165 in) was required by FDOT specifications (FDOT, 2012). A woven geotextile with AOS equivalent to No. 40 sieve was used in permeability testing. Accumulation of fines in the filter fabric mesh can greatly impede the flow of water passing from the aggregate into the natural soil, as a result,

decreasing the overall performance of the entire subsurface drainage system. This study investigated the flow rate of RCA with three variable AOS woven filter fabric meshes purchased from TWP, Inc. To cover a wide variation of soil types, RCA with mesh AOS of 0.007, 0.015, and 0.033 in. (corresponding to the % open of 29, 36, and 63, respectively) were tested. The specifications of the filter fabric used in this study are presented in Table 6.

Table 6: Geotextile specification

Part Number	^a Mesh (# of openings / in.)	^b Wire dia. (in.)	^c Opening (in.)	^d Percent open	^e Roll width (in.)	^f Weight (lb / ft. ²)
070X070S0065W48T	70	0.0065	0.007	29	48	0.07
040X040S0100W36T	40	0.0100	0.015	36	36	0.28
024X024S0085W60T_BLK	24	0.0085	0.033	63	60	0.11

^a Number of openings per linear inch measured from the center of one wire to a point one inch distance

^b The thickness of the wire in inches.

^c The distance between two adjacent parallel wires in inches.

^d The proportion of open space in section of screen expressed as %

^e Roll width in inches.

^f Weight of one square foot piece of mesh

A constant head permeability test was considered suitable for large aggregates such as No.4 gradation. Constant head permeability testing applies Darcy's Law to determine the permeability of the porous media. The formula for the coefficient of permeability (k) with the constant head test is shown below:

$$k = \frac{Q \cdot L}{A \cdot h \cdot t} \quad (1)$$

where k = coefficient of permeability (cm/s), Q = volume of discharge collected in time (t) (cm³), L = length of the specimen (cm), A = cross-sectional area of the specimen

(cm^2), h = head, difference in elevation of head tank and tailwater tank (cm), and t = time to collect the discharge.

Figure 5 presents a schematic diagram of the constant head permeability test setup. The test setup consists of a permeameter with RCA specimen and filter fabric on the bottom, constant-head tank, constant-head tail water tank, and recycling tank. A constant-head test using recirculating water was chosen over a falling-head test procedure to accommodate the faster flow of water expected to pass through the porous RCA samples. This test method best simulates the actual condition of a subsurface drainage system, where infiltrating runoff water may continuously carry fines or sediment into the filtration aggregate.

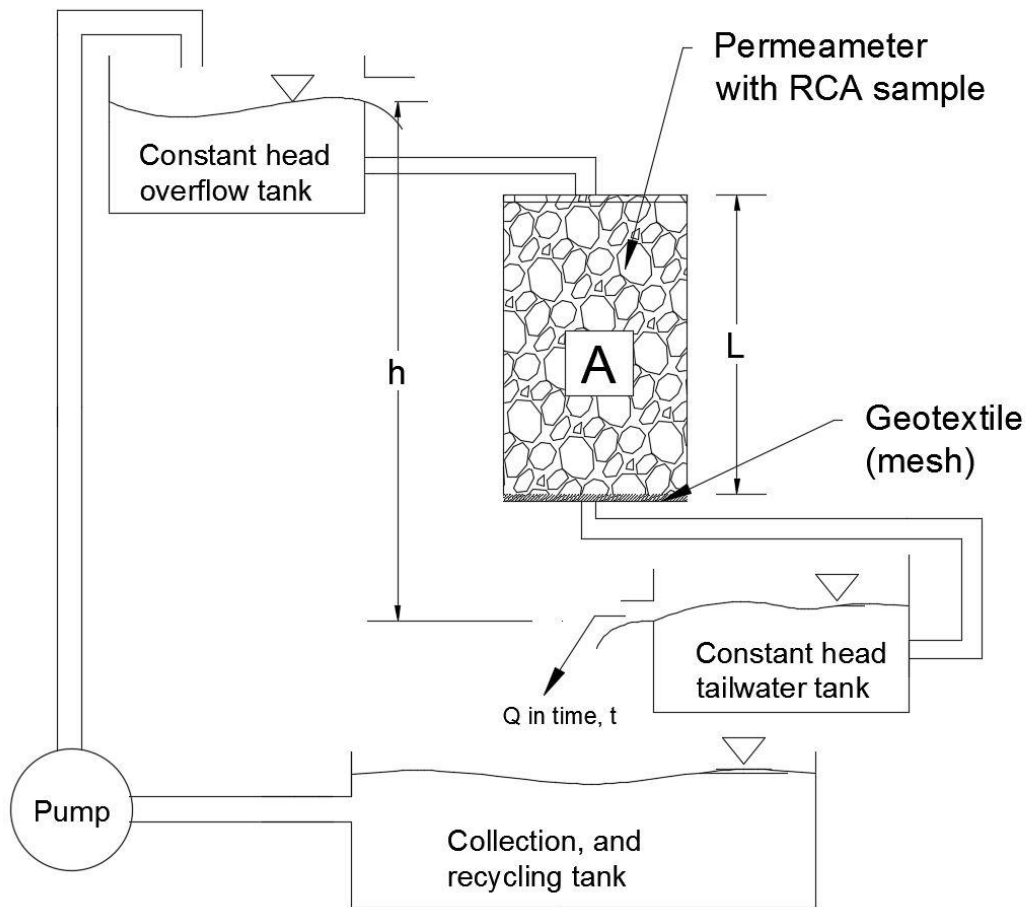


Figure 5: Constant head permeability test setup

Previous studies performed by Nam et al (2015) have shown that the size of the permeameter and tubing used, has a substantial impact on the measured discharge and corresponding coefficient of permeability. In an effort to allow a sufficient amount of water to flow through the RCA course aggregate, a 23-cm diameter permeameter connected with 12-mm diameter rubber tubing was used in our permeability test setup, which is the optimized setup identified by trial and error tests. For all permeameter tests, a constant head was kept at about 35-cms and averaged flowrates were calculated by measuring

the volume of water exiting the permeameter over 30 second time intervals. These flow rates were used in the analysis of the overall performance of subsurface drainage systems and how the accumulation of fines from the RCA affected the filter fabric.

In order to simulate the long term use of RCA used as a subsurface drainage filter, permeability tests were performed on RCA samples constantly over 100 day intervals. Permeameter testing under varied hydraulic gradient were tested at both initial and final stages because, unlike fine grained soils, RCA No. 4 gradation causes high flow velocity, thus the change of hydraulic gradient significantly affects the permeability coefficient. In addition, three separate RCA samples with 0, 2, and 4% addition of fines (passing the No. 200 sieve) were each tested using the apparatus shown in Figure 5. Flow rates were then measured from each permeameter at approximately the same time of day, 5 days a week. These percentages are based on FDOT specification, section 901-1.2, which states that coarse aggregate may not have more than 1.75% fines at source, or 3.75% at point of use for L.A. abrasion values of 30 or greater. Since the percent fines is limited by the FDOT standards, it will be beneficial to see how the clogging potential and flow rate of the RCA may be affected when fines fraction exceeds the standard. The closed system and recirculation of fines also will simulate the “worst-case” design scenario where fines from surrounding soils enters the RCA system. However, unlike RCA used in an actual subsurface drain, this long term clogging test will only simulate the physical generation and accumulation of fines—not clogging due to calcite precipitation. Further research through monitoring RCA in an actual in-situ subsurface drain is suggested to

see how both physical and chemical fines may accumulate over time and decrease the performance of the drainage system.

In order to study the influence that filter fabric mesh opening size has on RCA fines accumulation, permeability tests were performed using all three samples of RCA with varying filter mesh apparent opening size (AOS). A cut section of the mesh filter fabrics was secured into the bottom of the permeameters using silicon caulking around the edges. The silicon insured that all water flowing through the aggregate and out of the permeameter, must pass through the filter fabric. The flow rate was then monitored on set intervals over 24 hours for each sample. The same permeameter and tubing was used in this experimental setup, and the water was also recirculated as it was in the long-term monitoring test. This experimental setup of the permeameter was chosen to simulate the flow path of infiltrating water in an actual subsurface drainage system.

Permissible flow rates were measured in RCA samples with 0%, 2%, and 4% fines addition. Figure 6 shows the results of each sample test in the form of normalized flow rate over a 100 day period. By normalizing the data, we can easily see the overall decrease in flow rate (i.e. performance) of the RCA's drainage capability. All three % fines samples follow a linear degradation trend.

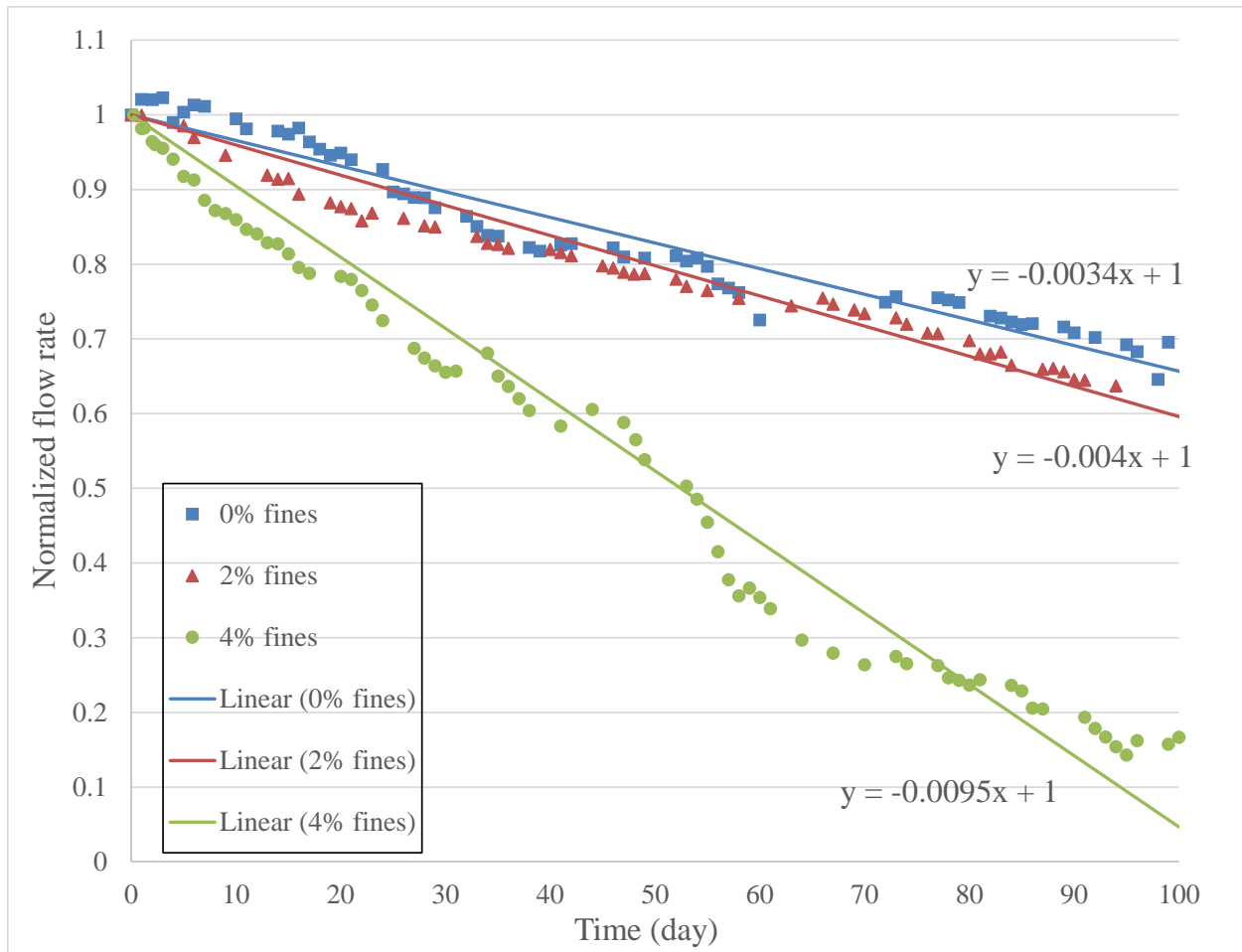


Figure 6: Long term flow rate monitoring

Over the 100-day testing period, the flowrate of all three samples were reduced through the process of clogging in the geotextile through the recirculation of water. The constant head of recycled water on the closed system allows us to establish that clogging of the geotextile is caused by the either physical or chemical deposition of fines, or calcite. Samples with 0% and 2% fines show a comparably slow reduction in flow rate and a total loss in performance of about 34% and 40%, respectively. The sample with 4% fines showed a greater overall reduction in flowrate in the 100 days. Its initial flow rate of 11.5

cm³/s was reduced to 3.2 cm³/s at the end of the 100 day testing period-- roughly a 73% reduction in flow. The increase in addition of fines will accelerate the rate of clogging in the geotextile and overall decrease the performance of RCA as a subsurface drainage material.

Permeability testing on all three samples was measured under varied hydraulic gradient at both initial and final stages. Since the 4% fine sample caused a significant reduction in the long-term measurement, a higher frequency of measurements was conducted during this test (at 0, 44, 85, and 100 days) and presented in Figure 7. It was shown that the coefficient of permeability decreases as the hydraulic gradient increases. Compared with the measurements at 0 and 44 days, the coefficient of permeability measured at 85 and 100 days exhibited an anomalous curve shift, showing a slight increase at the hydraulic gradient from 2.02 to 2.52. In addition, the coefficient of permeability at 44 and 85 days shows apparent reduction at all levels of hydraulic gradients. These phenomena are likely due to the accumulation of fines on geotextile, resulting in “irregular” measurements.

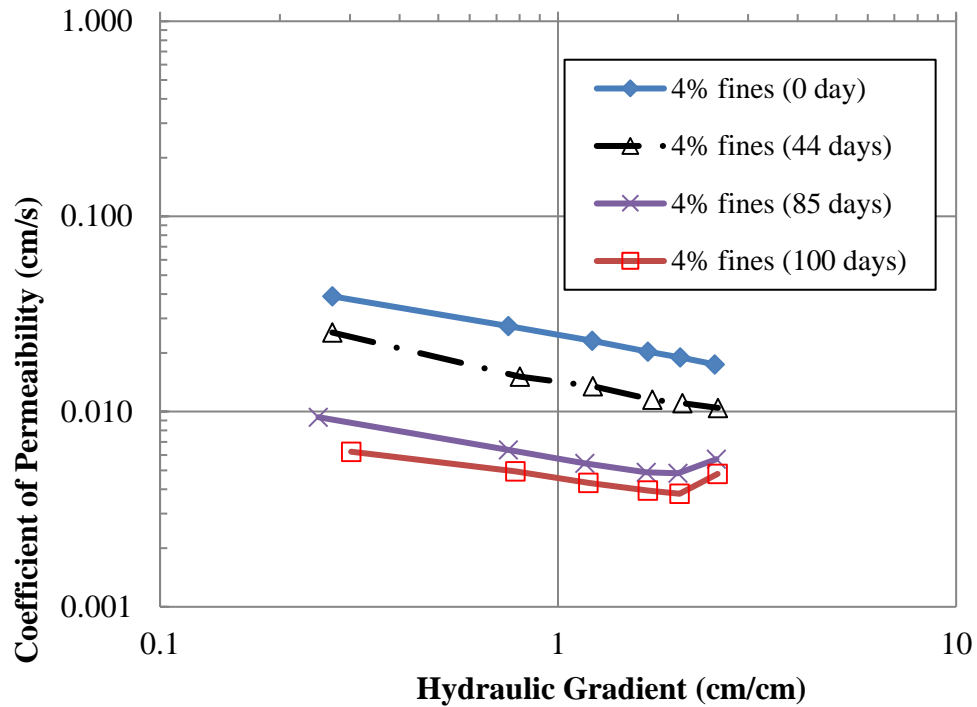


Figure 7: Flow rate measurements over time under varied head

Recall that flow rates through the varying percent fines samples of RCA were measured using three different filter fabrics of varied AOS. Flow rates were measured at the start of testing (within an hour) and after 24 hours of continuous pumping of water through the permeameter. The permeability test used in this procedure was of exact dimensions and head level of the aforementioned long-term permeability tests. Figure 8 shows the flow rate measured after 24 hours for each percent fines RCA sample and varying AOS of fabric. Samples with smaller percent of fines had higher flow rates over all three fabric AOS. For the larger mesh openings (36% and 63%), the flow rate seems to be independent of the fines content. Samples with 0% and 2% fines addition also showed negligible decrease in flowrate after 24 hours, compared to the 4% fines sample which

showed almost a 10% decrease in flowrate in the 63% AOS fabric. These results suggest that there is a limit to the amount of fines that are acceptable for maintaining the flow rate. Once fines start to accumulate on the fabric, the fabric effective AOS is decreased, thus hastening the entrapment of fines. Maintaining the flow rate with accumulation of fines on the filter fabric also limits the acceptable AOS to 36%.

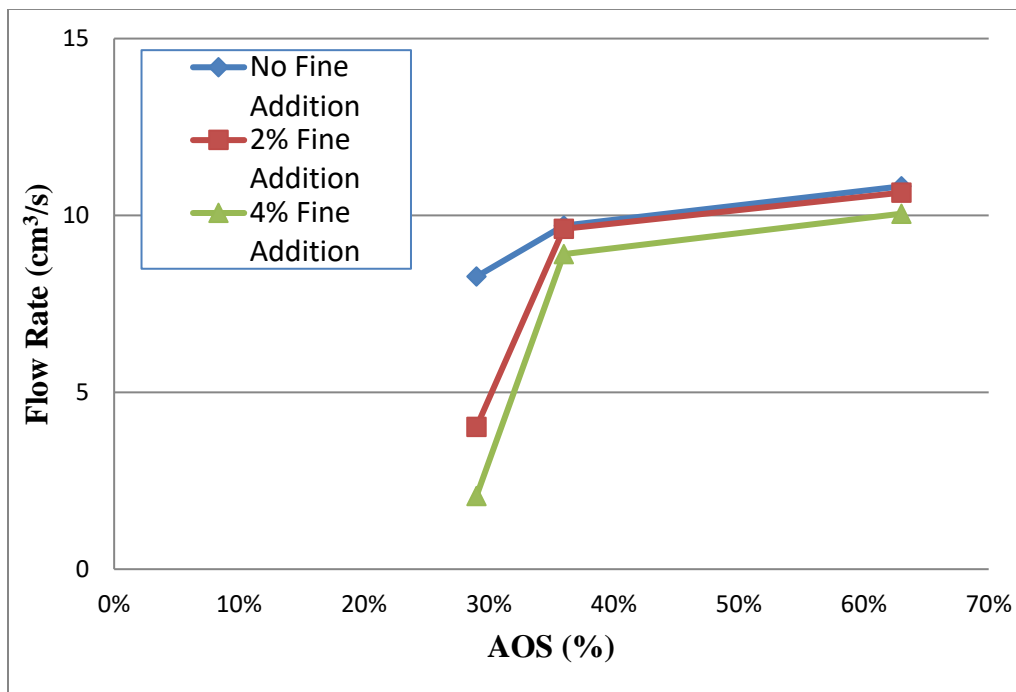


Figure 8: Flow rate as a function of fine addition and AOS.

Short and long term constant head permeability testing was implemented in order to investigate the degradation in performance of RCA simulated in an in-situ drainage system. Conclusions drawn from this study are summarized below.

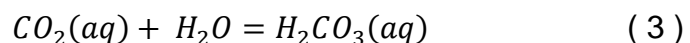
- The permissible flowrate of water through the RCA aggregate is greatly influenced by the amount of fines present. RCA samples tested with 0% and 2% addition did

not show significant decrease in flow rate considering the “worst case” simulation with recirculation of fines. The sample with 4% RCA fines addition, however, showed a decrease in flow of almost 90% over the 100 day testing period. Therefore, it is recommended to limit the fine content at job sites to less than 2% by weight. Washing aggregate at the job site prior to installation in the subsurface drain should also be considered to decrease the amount of fines entering the drainage media.

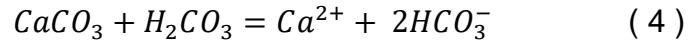
- Mesh size or apparent opening size (AOS) of filter fabric surrounding the drainage aggregate has a great impact on the clogging potential of the subsurface drain. Larger AOS meshes appear to allow similar flow rates independent of the amount of fines in the system. This suggests that the decrease in flowrate is due to clogging in the geotextile and not fine accumulation within the aggregate voids. Therefore, the authors recommend that a minimum permeability standard for filter fabric be considered in subsurface drainage applications.

Chemical Background on Calcium Carbonate Precipitation

Subsurface environments naturally contain CaCO_3 -rich limestone which, when exposed to rainwater, can dissolve and then precipitate calcite. Rainwater entering the subsurface environment is in equilibrium with the carbon dioxide, which dissolves to form carbonic acid as seen in Equations 2 and 3.



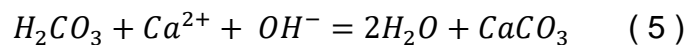
As the rainwater passes through the environment, the limestone is dissolved by the carbonic acid (Equation 4).



The dissolution of limestone introduces calcium ions to the solution.

When RCA is utilized in a subsurface drainage system, the chemistry will change from solely dissolution to dissolution followed by precipitation. RCA, like limestone, is rich in calcite ($CaCO_3$), but also contains portlandite ($Ca(OH)_2$). The dissolution of RCA will then result in the introduction of calcium ions (Ca^{2+}) as well as hydroxide ions (OH^-) from the portlandite, which will produce calcium-rich waters and precipitate calcite when exposed to the atmosphere.

The subsurface environment of a pavement system does not comprise carbon dioxide due to the overlying pavement structure. As a result, subsurface portlandite dissolves in the pore waters, but does not precipitate calcite. The drainage system or rainwater may introduce carbonic acid to the system, which will react with the dissolved calcium and hydroxide ions (Equations 1 and 2) to precipitate calcite, according to Equation 4.



CHAPTER THREE: PREVIOUS STUDY ON CALCITE PRECIPITATION OF RCA USING PROTOTYPE ACP METHOD²

Objective

The objective of this study is to evaluate the performance of RCA for use in French Drain systems. No. 4 graded RCA will be tested using the ACP procedure to investigate its calcite precipitation potential.

Materials

Chemical Properties of RCA

RCA from a C&D waste facility in Orlando, FL was A sample taken from the No. 4 graded RCA was ground into fine particles using a steel ball mill. The fines were chemically characterized using the Energy Dispersive X-ray (EDX) and X-ray diffraction (XRD) tests following ASTM C295 (ASTM , 2012). For chemical analysis, the RCA fines were ground using the Los Angeles abrasion machine and sieved through a No. 200 sieve, as shown in Figure 9. The EDX analysis (Table 7) shows that RCA mostly comprises carbon, oxygen and calcium, with traces of aluminum and silicon. The XRD analysis (Figure 10) shows that these elements mainly exist in the form of calcite (CaCO_3) and quartz (SiO_2), but no portlandite.

² This chapter includes previously published content.

McCulloch, T., Kang, D., Shamet, R., Lee, S.J., Nam, B.H. (2017). "Long Term Performance of Recycled Concrete Aggregate for Subsurface Drainage." *Journal of Performance of Constructed Facilities*, 31 (4), 4017015



Figure 9: Recycled concrete aggregate (left) and ground RCA fines (right).

Table 7: EDX results for RCA

Element	Test Values (Percent by weight)
Carbon	20.98
Oxygen	37.43
Aluminum	3.67
Silicon	3.68
Calcium	34.24
Total	100

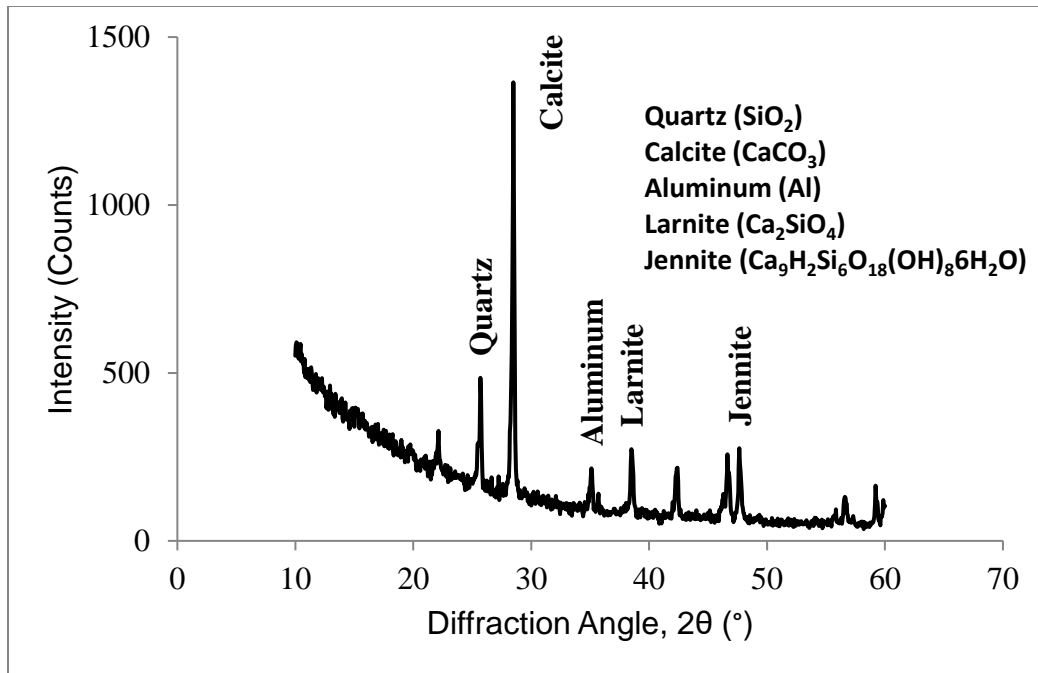


Figure 10: XRD analysis of RCA (Kim et al 2014)

Considering no portlandite, the RCA sample used in this study may be stored outside for a long period of time; thus, portlandite has already reacted with air and moisture. It is important to note that the original RCA source and location can greatly affect its physical and chemical properties. Concrete products made from different raw materials, mix proportions, and structural uses, may significantly affect the cement hydration product. The RCA source was unable to verify the original structural use of the concrete before it was crushed and sold. Figure 9 shows the RCA as-is alongside of the ground RCA fines. Upon visual inspection of the RCA, it is apparent that the aggregate supplied consists of a variety of original concrete products.

Methods of Investigation

The Accelerated Calcite Precipitation (ACP) Test Procedure, proposed by Nam et al. (2016), was used to investigate the long term performance of RCA for calcite precipitation. RCA is submerged in water, to which CO_2 is continuously added at a pH of approximately 6.0. When CO_2 is added to the water, H_2CO_3 is formed, which dissolves CaCO_3 in solution (releasing Ca^{2+} ions). Water is then filtered from the RCA and the leachate is placed in an oven at 110°C . The leachate contains Ca^{2+} and HCO_3^- which react to form calcite. A high temperature is used to accelerate the calcite precipitation process. After the specified time, the leachate is removed from the oven and filtered then the resulting calcite is weighed to complete one cycle (Figure 11).

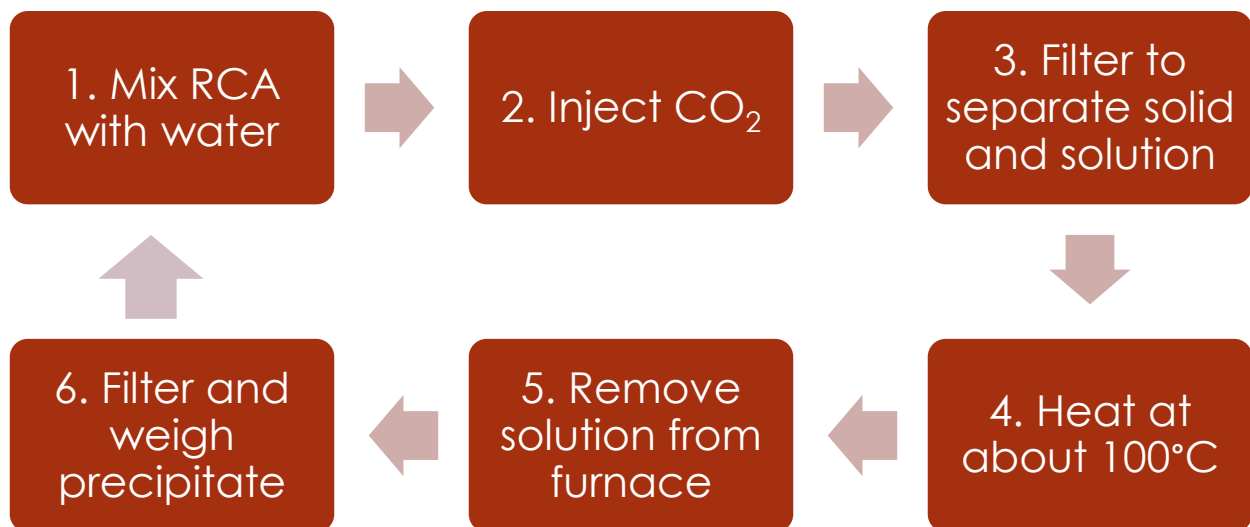


Figure 11: ACP procedure

Short-Term ACP Procedure

The purpose of the short-term ACP procedure is to evaluate the potential for calcite precipitation due to aggregate type and fines content. The sample (typically RCA) supplies calcium ions for precipitation only once. Filtered water is retained at the end of one cycle so that additional cycles can be performed on the water only to obtain any additional precipitate. Short term testing with the prototype ACP procedure was performed on RCA to compare calcite precipitation from limestone and RCA. Both samples with the same gradation were washed to remove attached fines. The procedure is outlined in Table 8.

Table 8: Short-term ACP procedure

Task	Description
Material preparation	Step 1. Obtain 2 kg of RCA (with specific gradation depending on applications) ¹ . Step 2. Place RCA in a container and fill with water (either tap or distilled water) until all aggregate is submerged. The same water-to-aggregate ratio should be used ² .
Extraction	Step 3. Inject CO ₂ into the water at a rate of 10 ft ³ /hr over 2 hours.
Filtration	Step 4. Filter out the water to remove RCA fines by using the ASTM D5907 filtration equipment.
Calcite formation	Step 5. Place the leachate (the filtered water) in an oven at 110°C for 4 hours.
Filtration	Step 6. Take the leachate out from oven and filter out again following ASTM D5907 to separate water and calcite precipitate.
Repeat the process	Step 7. Retain the filtered water. Repeat the process from Steps 3 through 7 for a total of 3 cycles, with the following change to Step 3. Inject CO ₂ into the retained water for 10 minutes ³ .

¹RCA can be used as base course or pipe backfill materials. For each application, the aggregate gradation specified in the applicable standards should be tested.

²The volumetric water-to-aggregate ratio of 1:3 is recommended.

³ The reduced injection time is recommended because the pH reaches a minimum within the first 10 minutes of injection.

Short term ACP method was also used to evaluate the effect of fines on calcite precipitation. Three kilograms of RCA was washed before 0, 2, 4 and 6% fines were added. The procedure in Table 8 was used with 3 kg of water and only two cycles of CO₂ injection.

Long-Term ACP Procedure

Calcite precipitation does not occur from only one interaction in nature. The long-term ACP procedure was developed to determine the total amount of calcite that can precipitate from the sample. RCA continuously supplies calcium ions until the precipitate yield becomes insignificant. The procedure is repeated with the same RCA and additional water, where the weight of the calcite is measured for each cycle. The detailed procedure of the long-term ACP method is presented in Table 9. Five kilograms of RCA was used for this experiment with 5 hours of CO₂ injection and 4 hours of heating.

Table 9: Long-term calcite precipitation simulation procedure for RCA (Nam, et al., 2016)

Task	Description
Material preparation	Step 1. Obtain 5 kg of RCA (with specific gradation depending on applications) ¹ . Step 2. Place RCA in a container and fill with water (either tap or distilled water) until all aggregate submerged. The same water-to-aggregate ratio should be used ² .
Extraction	Step 3. Inject CO ₂ into the water at a rate of 10 ft ³ /hr over 3 hours. A pH of 6.0 is recommended to be maintained during the injection.
Filtration	Step 4. Filter out the water to remove RCA fines by using the ASTM D5907 filtration equipment.
Calcite formation	Step 5. Place the leachate (the filtered water) in an oven at 110°C for 4 hours.
Filtration	Step 6. Take the leachate out from oven and filter out again following ASTM D5907 to separate water and calcite precipitation.
Repeat the process	Step 7. Reuse the RCA and fill with water in a container. Repeat the process from Tasks 2 through 6 until no calcite precipitation is produced ³ .

¹RCA can be used as base course or pipe backfill materials. For each application, the aggregate gradation specified in the applicable standards should be tested.

²The volumetric water-to-aggregate ratio of 1:3 is recommended.

³ The RCA will be repeatedly re-used to extract calcium ions until the calcium ion supply is depleted.

Results and Discussion

Short Term Calcite Precipitation Results

Table 10 and Figure 12 show two important trends. Firstly, the initial cycle of testing produced the highest calcite precipitation and the subsequent cycles produced one order of magnitude less calcite. Recall, cycles 2 and 3 underwent the ACP procedure on the filtered water from cycle 1 without any additional calcite source. Secondly, RCA yielded

twice as much calcite as the limestone. Nam et al had similar findings where hydrated cement paste in RCA produced more calcium ions than limestone.

Table 10: Comparison of calcite precipitation in limestone vs. RCA

LIMESTONE (2kg)	Calcite (g)	RCA (2kg)	Calcite (g)
Cycle 1 (2hr CO ₂ /20min setting/ 4hr oven):	0.5588	Cycle 1 (2hr CO ₂ /20min setting/ 4hr oven):	1.2608
Cycle 2 (10min CO ₂ /20min setting/ 4hr oven):	0.1802	Cycle 2 (10min CO ₂ /20min setting/ 4hr oven):	0.1036
Cycle 3 (10min CO ₂ /20min setting/ 4hr oven):	0.0051	Cycle 3 (10min CO ₂ /20min setting/ 4hr oven):	0.0935
Total	0.7441	Total	1.4579

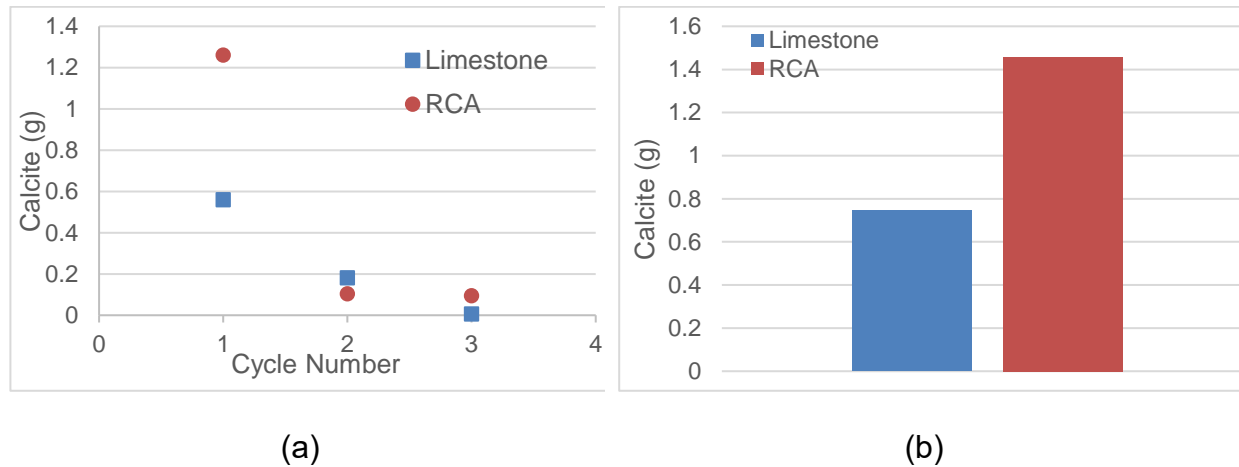


Figure 12: Results from short term ACP test (a) calcite precipitation from each cycle, (b) total calcite precipitation from each sample

Results from the fines experiment (Table 11) show that calcite precipitation increased with fines content. The sample with 6% fines produced twice as much calcite as the sample with 0% fines. It is also important to note that the sample with 0% fines produced 1.0181 g of calcite which indicates that the presence of fines is not a prerequisite for calcite precipitation, or that there may have been a few residual fines. Washing of the

RCA sample before adding fines was intended to minimize the initial fines content. Recall results from the permeability study (McCulloch, et al., 2017) which showed decreased flow rate over time due to increase in fines. These results provide insight to the clogging potential of RCA on geotextile filter fabric in French Drain applications. Clogging can be attributed to both the physical build up of fines and chemical precipitation of calcite.

Table 11 : Effect of fines on calcite precipitation in RCA

% fines	Calcite (g)
0	1.0181
2	1.5815
4	1.8502
6	2.0479

Long Term Calcite Precipitation Results

Figure 13 shows the mass of the calcite precipitate that was obtained from each cycle, and the overall decreasing trend with an increased cycle number. The trend shows that there is a limit to the precipitation of calcite in RCA, even with an unlimited supply of carbon dioxide. Similar observations can be made from Figure 14 where the cumulative calcite precipitation was plotted against the cycle number. A polynomial trend was observed because the mass of precipitated calcite followed a decreasing trend with increasing cycles. Based on the figure, the cumulative calcite precipitate will eventually obtain steady state where no more calcite precipitation would occur.

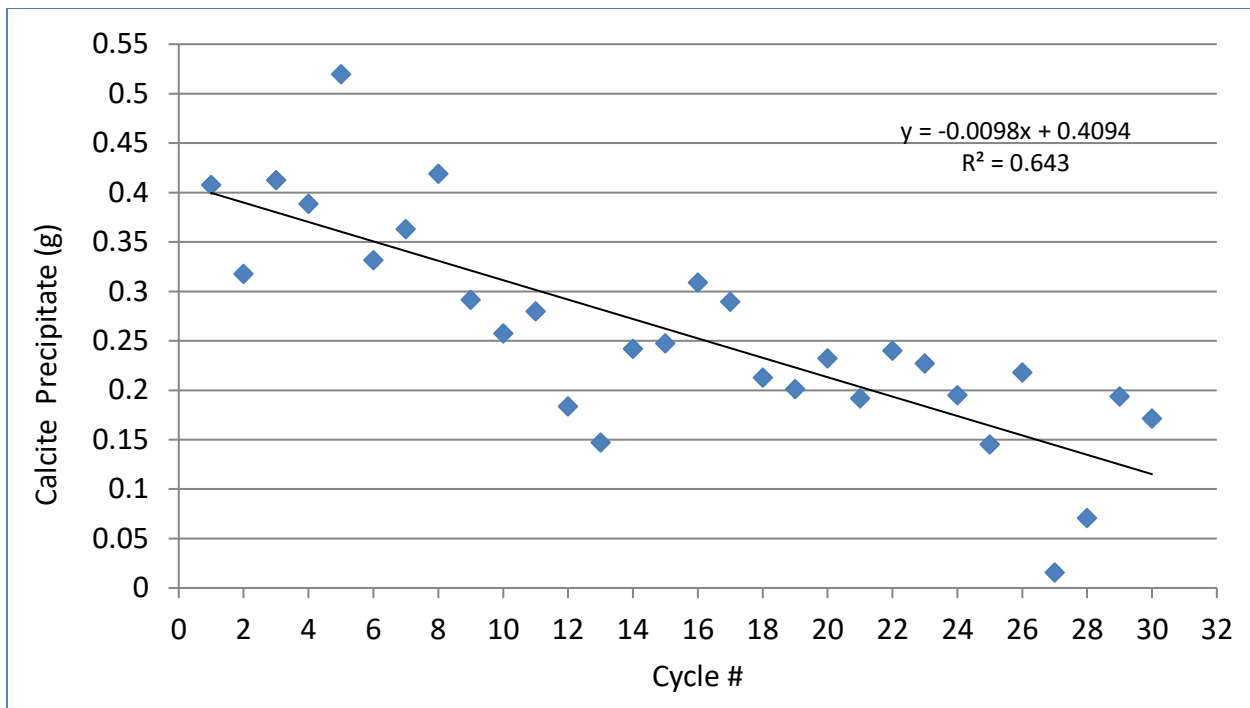


Figure 13: Resulting calcite mass from precipitation cycles

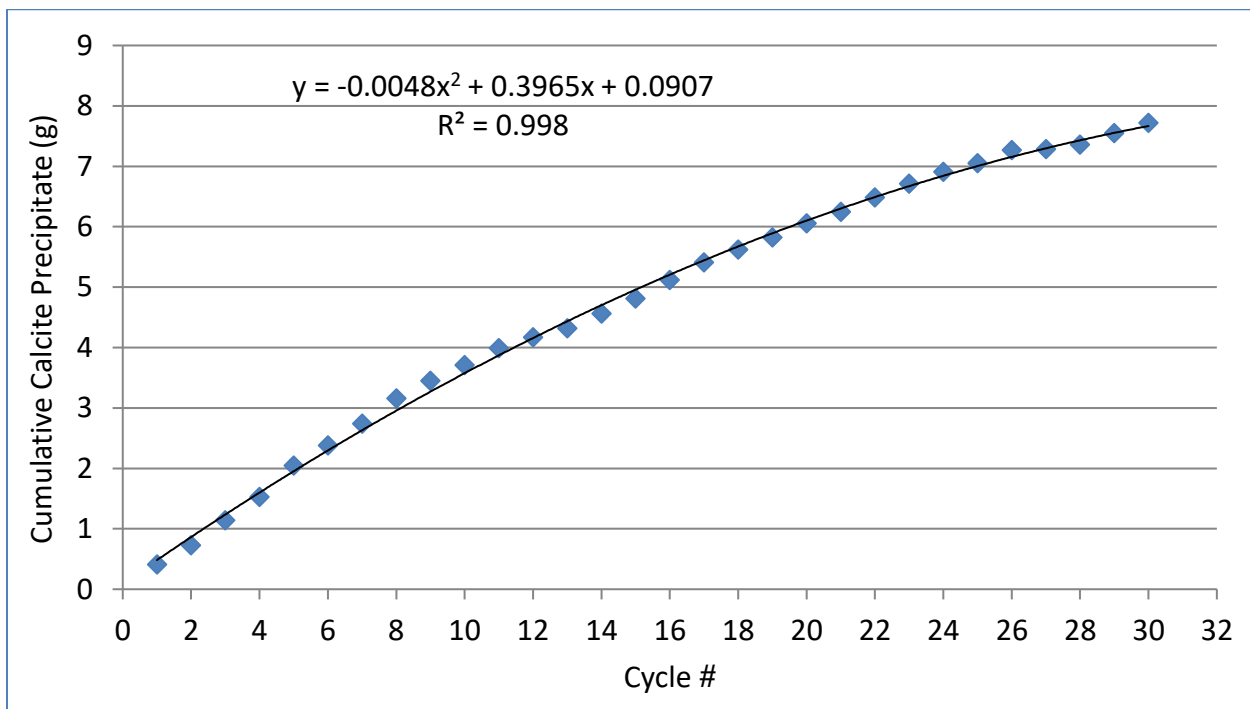


Figure 14: Cumulative calcite precipitate over 30 cycles.

The design of the ACP experiment simulates the chemistry that can occur in a subsurface environment. Calcite precipitation is a concern to researchers because the main chemical component of RCA is calcite as shown in Figure 10. The use of RCA as a subsurface drainage material would expose it to rainwater. The carbon dioxide in rainwater forms carbonic acid and causes dissolution of the calcite in RCA. These reactions are simulated by the ACP procedure as the carbon dioxide is injected into the RCA solution and allowed time to dissolve the calcite. The leachate that is collected during each cycle comprises calcium ions, carbon dioxide gas, as well as hydrogen and hydroxide ions which are the necessary reactants for precipitating calcite. These reactants would be present in a subsurface environment that contains RCA and is exposed to carbon dioxide and water. The next step of the experiment accelerates the calcite precipitation process by adding thermal energy to realize the potential for the following reactions to occur. The result shows that after 36 cycles, the 5kg RCA sample that was used in this experiment produced a total of 8g of calcite (i.e. 0.16% precipitated calcite).

Conclusions

The reuse of concrete as an aggregate material has been a popular topic of research over the past decade. The heterogeneity of RCA material properties makes it difficult to standardize as conventional material for state's department of transportation construction projects. This chapter evaluated the potential use of RCA as a subsurface drainage filter media. Chemical reaction of fines to calcite precipitation within the RCA was investigated in this study. Based on the findings, the conclusions drawn on how RCA might affect the performance of a subsurface drainage system are summarized below:

- Based on the short-term ACP procedure, calcite precipitation is more apparent in RCA than virgin limestone aggregate. Calcite precipitation potential increases with increasing fines content.
- Based on the long-term ACP procedure, the 5-kg RCA produced 8g of calcite precipitation, which is the “life-time” calcite under the worst environment. This small amount of calcite precipitation may have a negligible effect on the filter clogging.

CHAPTER FOUR: OPTIMIZATION OF THE PROTOTYPE ACP METHOD

Objective

The prototype ACP test method that was used to investigate the long-term performance of RCA in subsurface drainage systems provided insight into the calcium carbonate precipitation potential for No. 4 aggregate. There are varying factors that influence the reactions throughout the ACP procedure. These factors include calcium ion concentration, surface area, pH, heating temperature and heating time. The objective of this study is to maximize calcite precipitation by optimizing the prototype ACP method. Optimization in this study will be accomplished by investigating the effect of temperature and reaction time on the prototype ACP method.

Factors Affecting Calcite Precipitation in ACP Method

The calcium ion concentration depends on the material that is being tested. The sample has a finite concentration of calcium donor material such as calcite or portlandite. Limestone, for example, has calcite but not portlandite. Depending on the concentration of impurities, limestone samples can also have varying concentrations of calcite.

The exposed surface area of the sample affects the calcium ion concentration in solution. Once carbonic acid forms in the solution, it reacts with the surface of the sample to dissolve calcium ions in the solution. An increase in the surface area will increase the potential for this reaction to occur and will increase the potential for calcium ion dissolution.

Carbon dioxide-carbonic acid equilibrium depends on the pH of the solution. An increase in pH favors carbonate while a decrease in pH favors carbonic acid. Behring (2013) measured the pH during the ACP test and found that it changed at different points in the process. The pH averaged around 6.0 during carbon dioxide injection, increased to 6.47 after filtration and continued to increase to 6.78 during the 4 hours of heating (Behring, 2013). The 6.0 pH during carbon dioxide injection indicates the presence of a weak acid such as carbonic acid. The increase in pH after filtration indicates a shift toward an alkaline environment that favors the presence of bicarbonate. A further increase in pH favors the presence of carbonate. The pH can be varied by varying the concentration or length of time for carbon dioxide injection.

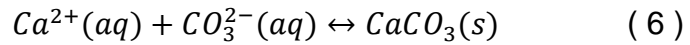
The rate of a reaction is influenced by temperature (Walas, 1959). For a normal reaction, the rate increases exponentially with temperature. The reaction rate can increase slowly with increasing temperature if the reactants are in different phases and the reaction is dominated by resistance to diffusion. Another type of behavior is demonstrated by explosions where the reaction rate slowly increases with temperature before the explosion and then shows a sharp increase in rate at the temperature of the explosion. The rate of adsorption increases in catalytic reactions with temperature but decreases at higher temperatures. This behavior is also evident in enzyme reactions where the enzyme is destroyed by high temperatures. The rate of some reactions is affected by simultaneous reactions that become significant with increasing temperature. There are also reactions

for which the rate decreases with increasing temperature. Most reaction rates exhibit normal behavior under the influence of temperature.

The objective of this study is to maximize the calcite precipitate yield for each cycle in the ACP procedure. The reaction rate will be optimized by varying the heating temperature and heating time. The effect of temperature and time on reaction rate is fundamentally explained by collision theory.

Collision Theory

William M. White used nitrogen and oxygen to explain reaction theory (White, 2013). This paper will use the same logic to explain reaction theory with the simplified reaction between calcium and carbonate.



White derived the equation for the rate constant of the reaction by considering two factors.

1. The number of collisions between the reactants (Ca and CO₃).
2. The fraction of atoms with sufficient energy to react.

Consider a calcium ion travelling with the combined radius, r , of the calcium ion and carbonate ion. The calcium ion travels a distance, d , to the carbonate ion at a velocity, v , in time, t . Assuming the calcium ion travels in a straight line to collide with the carbonate ion, it would cover a volume, V with the relationship

$$V = \pi r^2 d = \pi (r_{Ca} + r_{CO_3})^2 (vt) \quad (7)$$

The total number of collisions that will occur during this period is

$$c = n_{CO_3} \pi v t (r_{Ca} + r_{CO_3})^2 \quad (8)$$

where n_{CO_3} is the number of carbonate ions per unit volume. Equation 8 shows that the number of collisions depends on the concentration and velocity of the atoms in the solution, as well as the time. The rate of collisions, then, is

$$\dot{c} = n_{Ca} n_{CO_3} \bar{v} \pi (r_{Ca} + r_{CO_3})^2 \quad (9)$$

where n_{Ca} is the number of calcium ions and \bar{v} is the average velocity of the calcium and carbonate ions.

The next step is to determine the fraction of atoms that will have enough energy to overcome the electrostatic repulsion known as the barrier energy E_B . The fraction of molecules with sufficient energy to overcome the barrier energy and react is

$$n_{E>E_B} = e^{-\frac{E_B}{kT}} \quad (10)$$

where k = Boltzmann's constant and T = temperature

The number of collisions with enough energy to overcome the barrier energy is the rate of reaction which is given by multiplying Equation 9 by Equation 10.

$$R = n_{Ca} n_{CO_3} \bar{v} \pi (r_{Ca} + r_{CO_3})^2 \left(e^{-\frac{E_B}{kT}} \right) \quad (11)$$

The distribution of velocities of the molecules in a gas given by Maxwell-Boltzmann's law is used to approximate the velocity between the calcium and carbonate ions.

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}} \quad (12)$$

where the reduced mass, $\mu = \frac{m_{Ca} m_{CO_3}}{m_{Ca} + m_{CO_3}}$

Substituting Equation 12 into Equation 11,

$$R = n_{Ca}n_{CO_3}\pi(r_{Ca} + r_{CO_3})^2 \sqrt{\frac{8kT}{\pi\mu}} \left(e^{-\frac{E_B}{kT}} \right) \quad (13)$$

From Equation 13, it is clear that the reaction rate depends on the concentration of the reactants, the temperature and the barrier energy, which is also known as the activation energy. The reaction rate, then, increases exponentially with increasing temperature, but decreases with increasing activation energy. The activation energy is specific to the reaction.

Another demonstration of temperature's influence on reaction potential is the Maxwell-Boltzmann distribution which relates the energy of particles in a system to the temperature. Figure 15 represents the energy of a system at two different temperatures where T_2 is greater than T_1 . The system at T_1 has a higher number of molecules with lower energy while molecules in the system at T_2 have higher energy. E_a is the activation energy for the reaction. The significant observation from this figure is that the system at T_2 has more molecules with energy that is high enough to overcome E_a than the system at T_1 . The implication, then, is that the system at T_2 has the potential for a higher yield in the case of a precipitation reaction. The precipitation yield from the ACP method is expected to increase by increasing the reaction rate with higher reaction time and temperature.

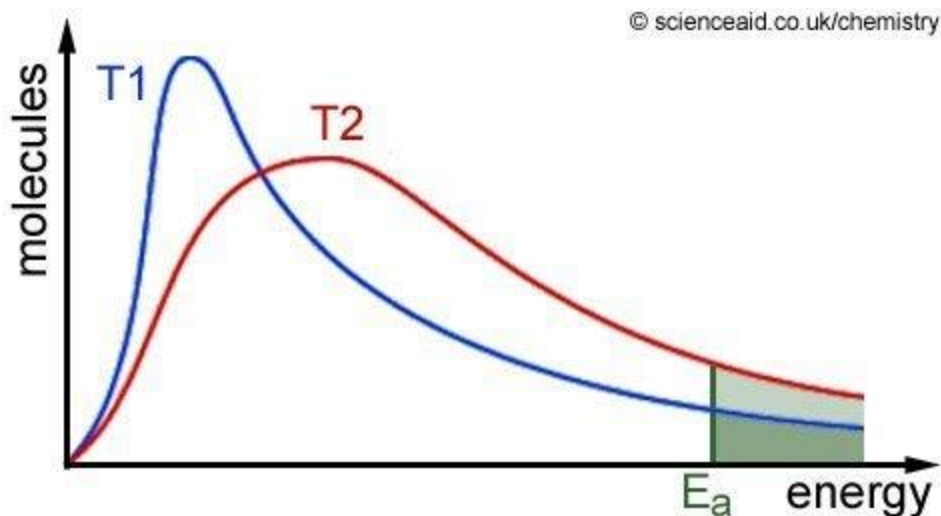


Figure 15: Maxwell-Boltzmann diagram (ScienceAid, 2017)

Method of Investigation

The Accelerated Calcite Precipitation (ACP) test procedure proposed by Nam et al. (2016), simulates the process by which calcium carbonate precipitates in nature (Figure 16 and Figure 17). The ACP method begins with submerging the calcium source (ex. RCA) in water (Step 1). The bubbling of CO_2 is analogous to Equations 1 and 2 where CO_2 , in equilibrium with rainwater, dissolved to form carbonic acid (Step 2). The carbonic acid in the solution dissolves the RCA as with limestone in nature (equation 2, 3). The RCA is then filtered from the solution (Step 3). The leachate is heated to accelerate calcium carbonate precipitation (Step 4). After the appropriate heating time, the leachate is taken out of the furnace to cool before the precipitate is filtered (Step 5). The filter paper is weighed on the Digiweigh DWP-B2004 (Figure 18) while the leachate cools. The

leachate is then filtered and the precipitate is dried at room temperature. The precipitate is weighed after at least 24 hours of drying (Step 6).

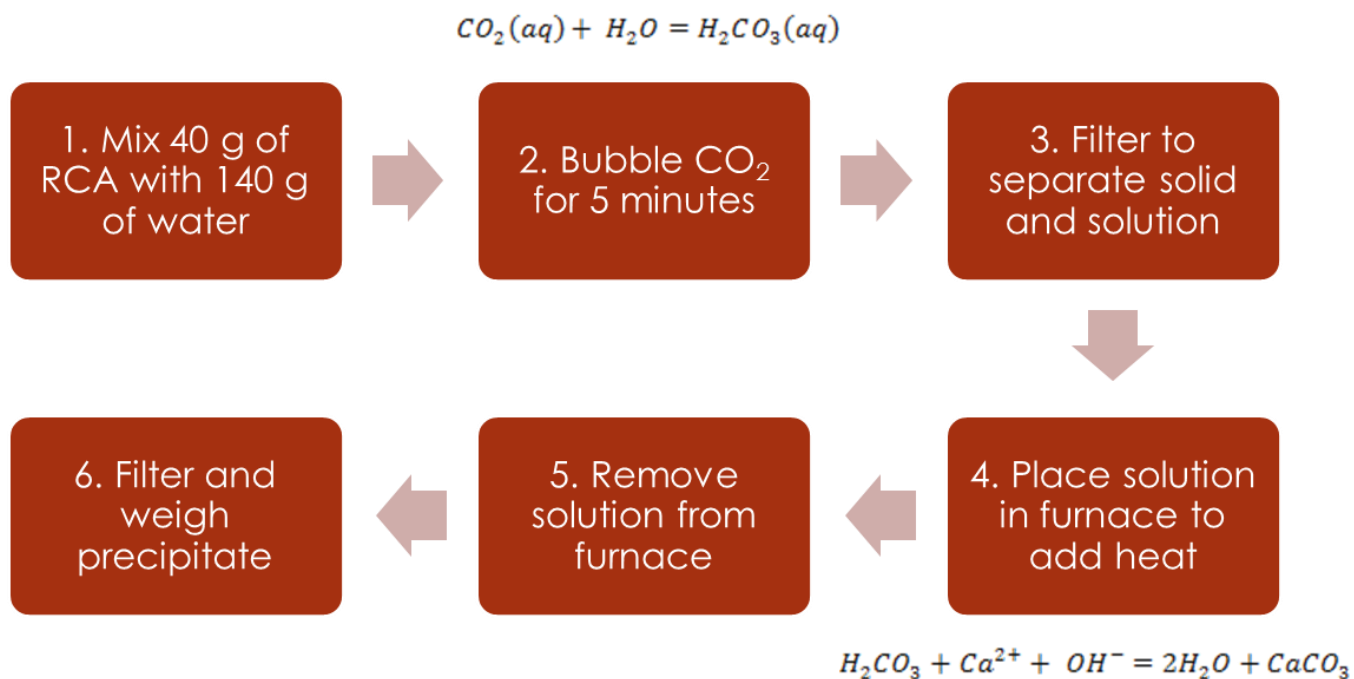


Figure 16: ACP procedure

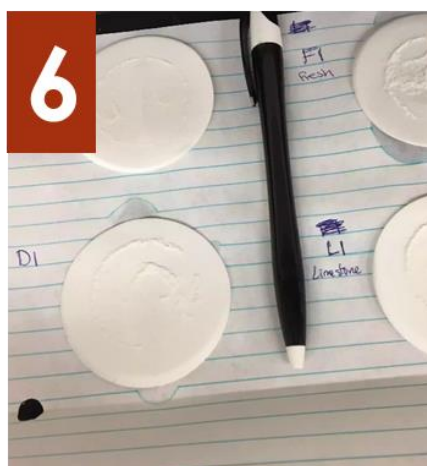
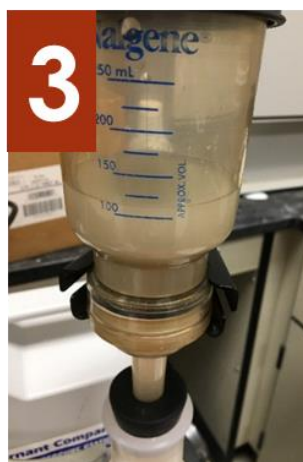


Figure 17: Visual representation of the ACP procedure with reference to each step



Figure 18: DigiWeigh Laboratory Scale

The DWP-B2004 by DigiWeigh (Figure 18) was used to measure the precipitate. This balance has a ± 0.0001 g reproducibility. The mass of the precipitate was determined from the difference in the mass of the filter paper before and after the precipitate was filtered. The DWP-B2004 was calibrated with 200 g standard mass per the user manual. The specifications for the DWP-B2004 can be found in Appendix B.

The ACP test procedure was the basis for the optimization method. The RCA was ground in the LA abrasion machine with 6,000 cycles to produce fine RCA material. The purpose of grinding was to increase the surface area of RCA that interacts with the H_2CO_3 during the carbon dioxide injection. In this procedure, 40 g of ground RCA was submerged in 140 g of water and CO_2 was bubbled into the solution for 5 minutes. The liquid was filtered from the RCA and the leachate was placed in the furnace for a heating time that varied

from 30 minutes to 24 hours and temperature of either 110°C, 75°C or 50°C. The purpose of heating the sample was to accelerate the precipitation reaction and as a result, room temperature was not considered for this experiment. The precipitate was filtered from the solution, dried at room temperature and weighed at the end of the heating process.

Results

The calcium carbonate precipitation at 110°C for each value of heating time is shown in Table 12. Figure 19 shows that the calcium carbonate precipitation increased with time to 7 hours, stabilized between 7 and 17 hours, and then decreased slightly at 24 hours. The maximum mean value of calcium carbonate precipitation was 0.0194 at 7 hours, which resulted in 0.05% of precipitated calcium carbonate.

Table 12: Calcium carbonate precipitation at 110°C

Heating Time (hr)	Weight (g)	
	Sample 1	Sample 2
0.5	0.0110	0.0112
2	0.0139	0.0127
4	0.0203	0.0178
7	0.0174	0.0194
10	0.0159	0.0178
13	0.0141	0.0188
17	0.0178	0.0186
24	0.0148	0.0118

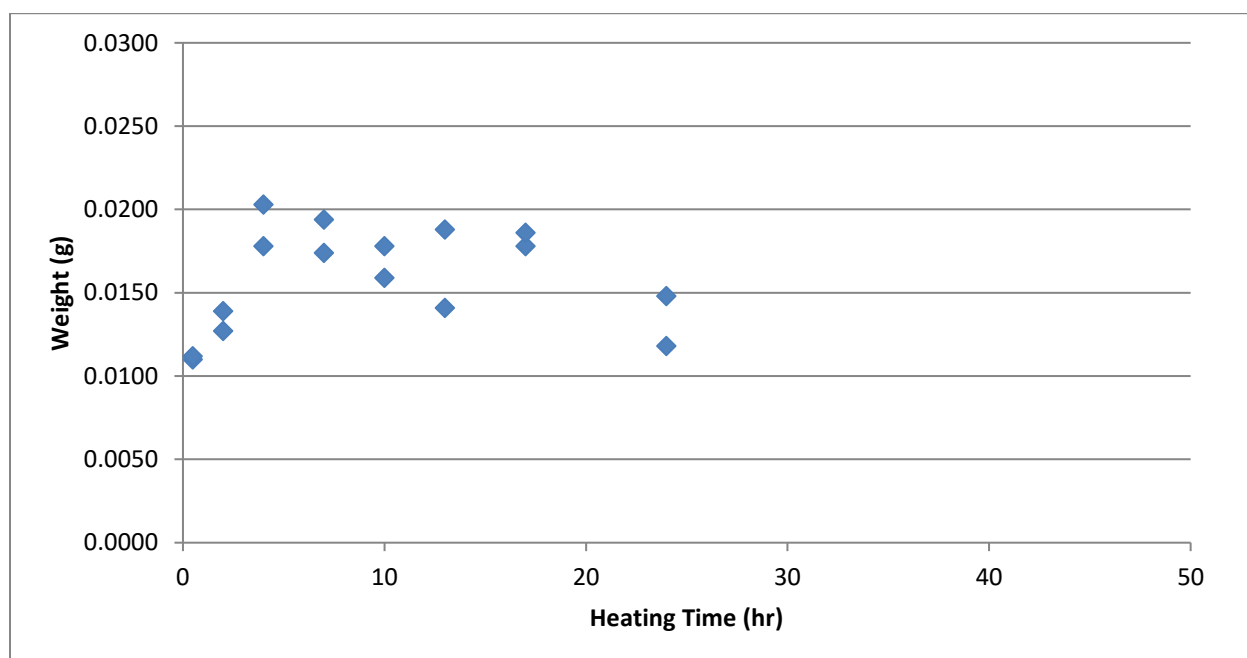


Figure 19: Calcium carbonate precipitation at 110°C

Table 13 shows the calcium carbonate precipitation at 75°C for each value of heating time. Figure 20 depicts the results in Table 13. The results for 75°C show a different trend from 110°C. The calcium carbonate precipitation increased for heating times up to 4

hours, slightly decreased for heating times between 4 hours and 13 hours, then peaked at 17 hours before it decreased to 48 hours. The maximum mean value was 0.0267 g which results in a 0.07% of precipitated calcium carbonate.

Table 13: Calcium carbonate precipitation at 75°C

Heating Time (hr)	Weight (g)	
	Sample 1	Sample 2
0.5	0.0130	0.0114
2	0.0154	0.0173
4	0.0192	0.0149
7	0.0202	0.0178
10	0.0176	0.0156
13	0.0187	0.0163
17	0.0267	0.0246
24	0.0195	0.0228
48	0.0143	

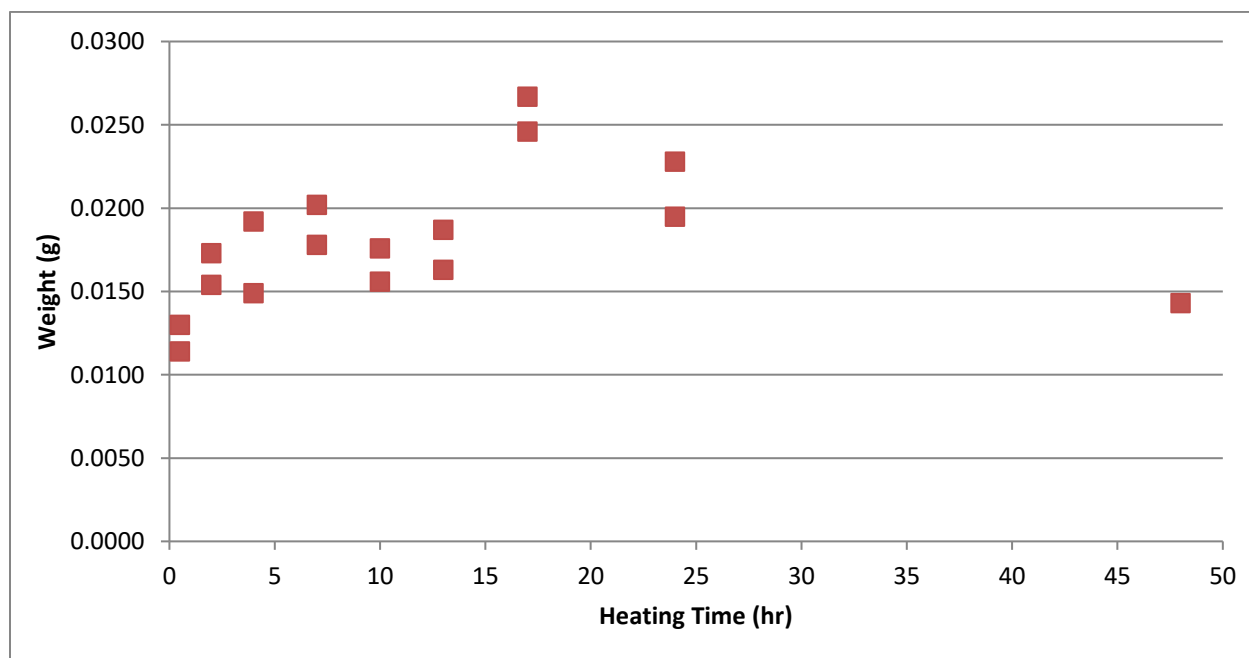


Figure 20: Calcium carbonate precipitation at 75°C

The results for the calcium carbonate precipitation at 50°C are shown in Table 14 and depicted in Figure 21. Experiments that were performed at 50°C showed an increase in calcium carbonate precipitation with heating time, even to 48 hours. The maximum value was 0.228 g at 24 and 48 hours which resulted in 0.06% of precipitated calcium carbonate.

Table 14: Calcium carbonate precipitation at 50°C

Heating Time (hr)	Weight (g)	
	Sample 1	Sample 2
0.5	0.0080	
2	0.0083	0.0007
7	0.0153	0.0069
10	0.0115	0.0157
13	0.0244	0.0162
17	0.0155	0.0188
24	0.0180	0.0228
48	0.0228	

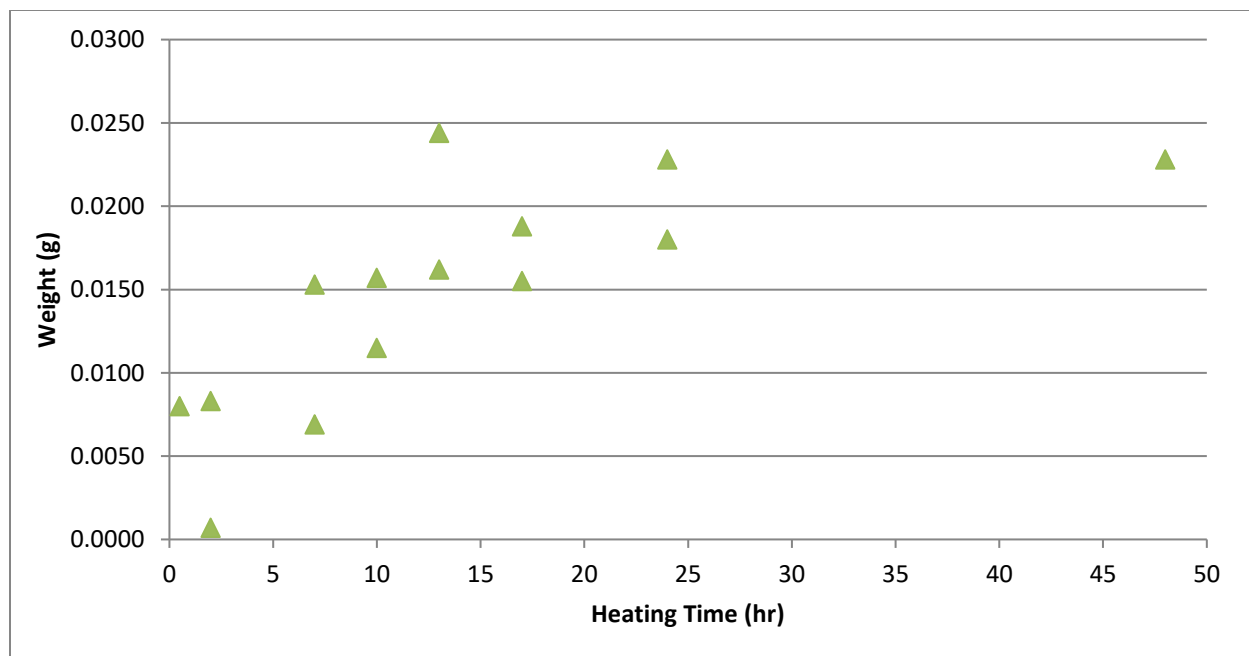


Figure 21: Calcium carbonate precipitation at 50°C

Figure 22 compares the calcium carbonate precipitation results for all heating temperatures. This figure shows that the calcium carbonate precipitation at the heating temperature of 75°C is the highest for 67% of the heating time values. At heating time values of 10 hours and 13 hours, the difference between the calcium carbonate precipitation value at 75°C and the maximum value are 0.003 g and 0.001 g, respectively, which is not significant. At 48 hours, the difference between the calcium carbonate precipitation value at 75°C and the maximum value at 50°C is 0.0085 g. The calcium carbonate precipitation value had decreased significantly from its maximum value at 17 hours. The value at 50°C had increased to the maximum value for that temperature.

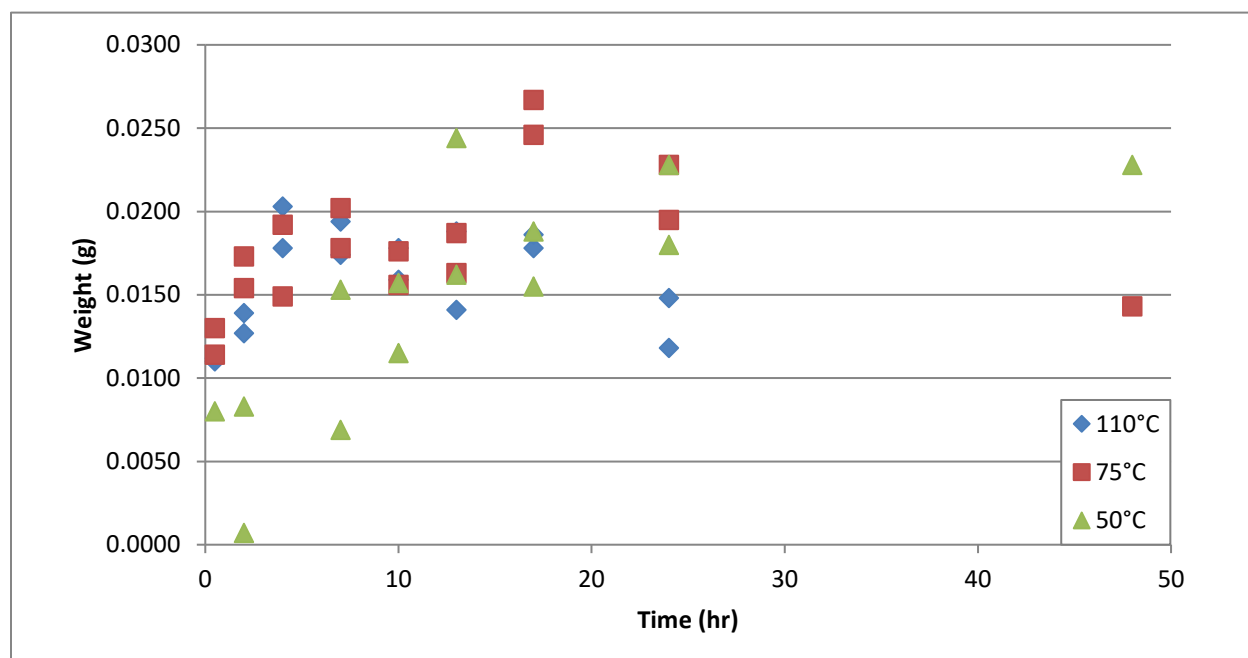


Figure 22: Summary of calcium carbonate precipitation results

Discussion

Consider Equation 8 which describes the collision theory. The number of collisions that occur within the solution depends on the concentration of the reactants, the velocity of the atoms, molecules and ions (particles), as well as the time allowed for the particles to move throughout the solution. The experimental method for this experiment was designed to have the same concentration for each sample by using the same weight of RCA and water, as well as the same time for carbon dioxide inundation. It is therefore safe to assume that the concentration of the reactants is the same for each sample. The variable factors would then be the velocity and time for collision.

The velocity of a particle is related to its kinetic energy. A high velocity indicates high kinetic energy and vice versa. Any energy supplied to or released from the system changes the kinetic energy of the particles within the system and therefore changes the velocity. The addition of heat energy, by increasing the temperature of the furnace, increases the kinetic energy of the particles in the system and increases the number of collisions. Figure 22 shows the precipitation at higher temperatures (75°C and 110°C) are generally higher than that of the lower temperature at 50°C, in part due to the higher energy supply. In fact, the calcium carbonate precipitation values at 50°C were the lowest for 62.5% of the heating time values. Figure 23 and Figure 24 show the variation of precipitation with increasing temperature for heating times of 2 hours and 10 hours. The precipitation at 75°C and 110°C is higher than at 50°C. This means that there is an increase in the number of collisions between particles in the systems with the higher temperatures for both heating times.

In addition to the velocity, the reaction time plays an important role in the probability of a collision. A particle moving at velocity, v , will need time to arrive at another particle before a collision can occur. Following the theory, an increase in reaction time will result in an increase of the number of collisions, assuming no energy is removed from the system. For the ACP method, the measured reaction time is the time that the sample is in the furnace. It is understood that the particles in the solution may begin to react during carbon dioxide inundation and continue to react during the cooling time. Those times are

predetermined and fixed for each sample, so the noteworthy variation in reaction time occurs when the sample is in the furnace. The heating time was intentionally varied for this experiment to determine an optimal time for calcite to precipitate. From the results in Figure 21, the general trend was an increase in precipitation with time for samples that were heated at 50°C. Samples that were heated at 75°C and 110°C began with an increase in precipitation with heating time, followed by a nominal decrease in precipitation (Figure 19 and Figure 20). At 75°C, there was a significant increase in precipitation for the 17-hour heating time, after which the precipitation decreased considerably with heating time. The samples that were heated at 110°C showed a slight decrease in precipitation with heating time after 17 hours.

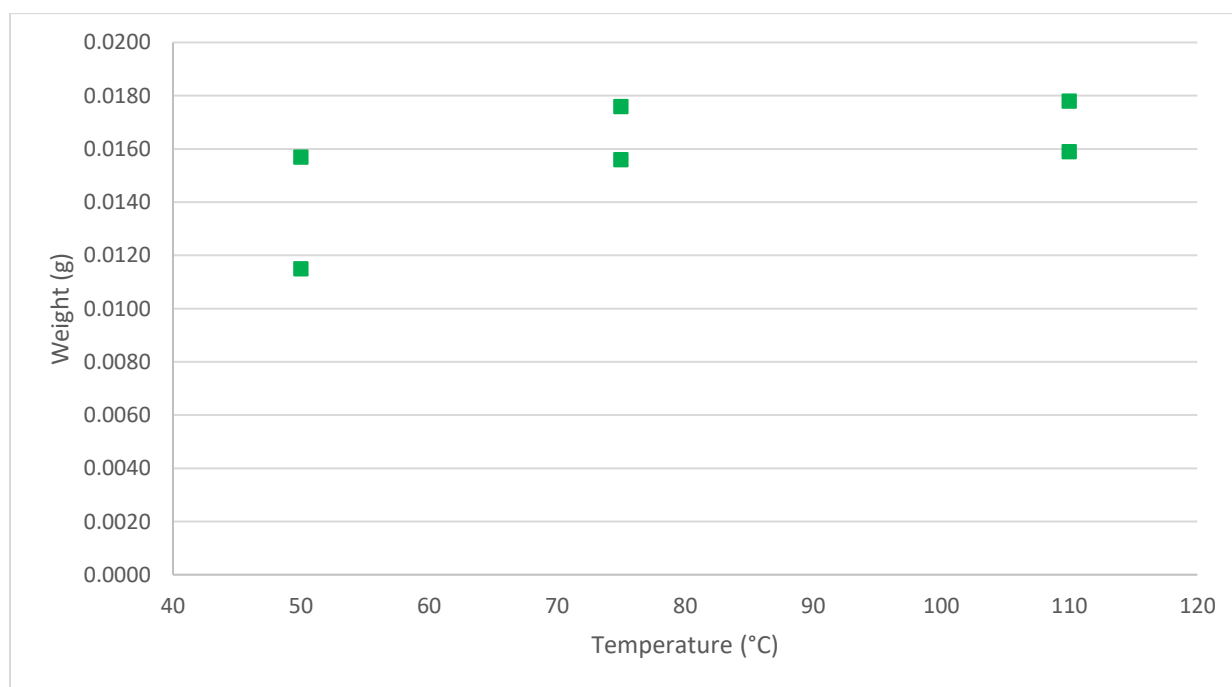


Figure 23: Variation of temperature with precipitate weight for 10-hour heating time

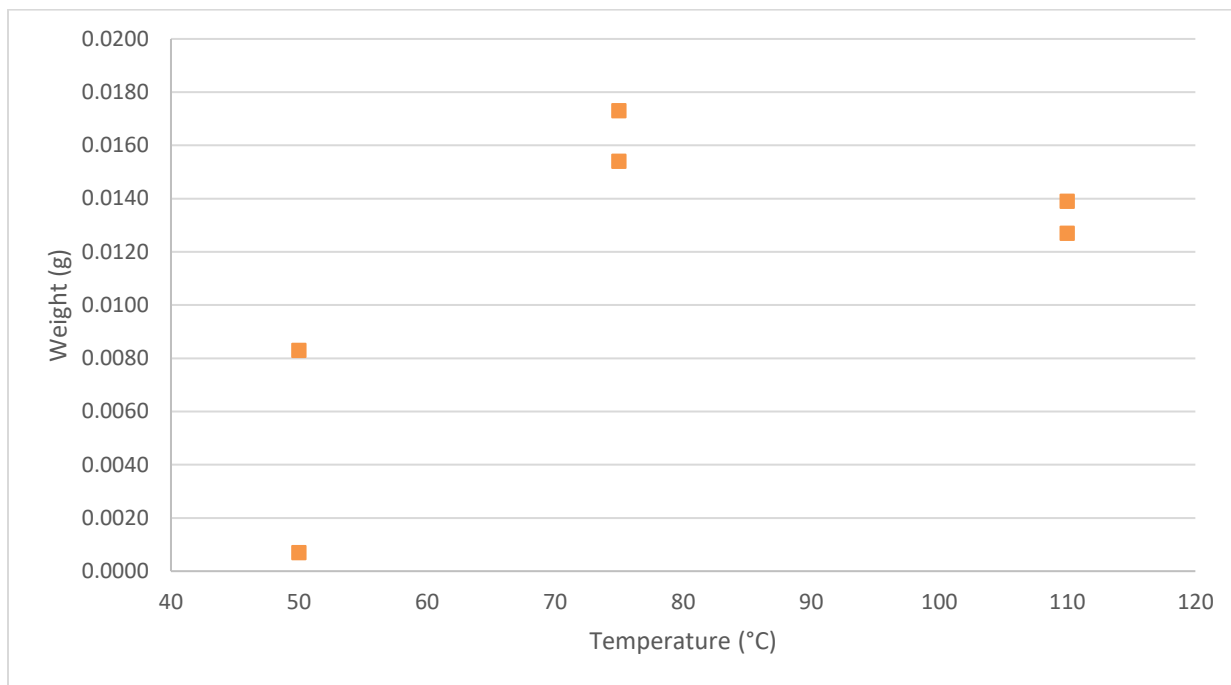


Figure 24: Variation of temperature with precipitate weight for 2 hour heating time

The number of collisions is only one factor in accelerating the calcite precipitation reaction. Each particle that collides needs to have enough energy to overcome the activation energy and to react with the other particle in the collision. The relationship in Equation 13 shows that the reaction rate depends on the activation energy and temperature of the system.

$$R \propto e^{-\frac{E_B}{kT}} \quad (14)$$

The Maxwell-Boltzmann distribution demonstrates that a system at a higher temperature has an increased number of particles with higher energy than a system at lower temperature. The consequence of the Maxwell-Boltzmann distribution is that there is a

higher probability that a reaction will occur at a higher temperature because more particles will have enough energy to overcome the activation energy.

Recall Equation 13. The reaction that results in the precipitation of calcite, for example, requires a certain activation energy. The activation energy for this reaction can be considered constant. The reaction rate, then, will be affected by the number of collisions and the temperature. As previously discussed, an increase in temperature will add heat to the system and energy to the particles in the system. The additional energy not only increases particle velocity, it also increases the probability of a reaction upon collision.

Following that logic, one would expect that all samples would have increased precipitation with increased reaction time and temperature. The data somewhat complies with that logic, but the precipitation at 75°C was greater than 110°C for most of the heating time values. The reaction most likely approached equilibrium, the point at which the reaction seems to stop. In reality, equilibrium is the point at which the rate of the forward reaction is the same as the rate of the reverse reaction. The equilibrium constant, K , is defined as the ratio of the forward and reverse rate constants, k_1 and k_2 , respectively. The equilibrium constant depends on the temperature and enthalpy of the system. For endothermic reactions ($\Delta H > 0$), the equilibrium constant increases with increasing temperature. For exothermic reactions ($\Delta H < 0$), the equilibrium constant decreases with increasing temperature. Figure 19 and Figure 20 indicate an exothermic reaction between calcium, bicarbonate and hydroxide ions with a decreasing equilibrium constant. The

measured precipitation at 75°C is greater than at 110°C for 66% of the heating time values. At 110°C, the forward reaction occurred for heating times below 4 hours, approached equilibrium for heating time values between 4 and 17 hours, before the reverse reaction occurred. At 75°C, the forward reaction occurred up to the 13-hour heating time value, and then the reverse reaction at the 24-hour heating time, with equilibrium occurring at heating time values in between 17 and 24 hours. At 50°C, the observed precipitation indicates the forward reaction for all heating time values without approaching equilibrium. The equilibrium constant is decreasing with temperature which denotes an exothermic reaction.

It is important to note that the equilibrium constant does not depend on reaction time. The longer reaction time will give the system an opportunity to arrive at equilibrium, where enough collisions have occurred with enough energy for the forward and reverse reactions to occur at the same rate. The samples that were heated for short times did not have enough time to approach equilibrium. The equilibrium constant, based on the equations, remains the same for a given temperature. The results do show a decrease in the heating time to approach equilibrium with an increase in temperature. At 50°C, the heating times up to 48 hours do not indicate an arrival at equilibrium. The decrease in the slope of the trend does indicate that equilibrium is being approached after the 24-hour heating time. At 75°C, equilibrium occurs between 13 and 24 hours of heating time. The decreased heating time value of equilibrium at the higher temperature is a result of the increased number of collisions with higher energy.

Conclusion

Optimization of the ACP method was accomplished by investigating the effects of temperature and heating time on the precipitation. Results showed that increasing the temperature increases the kinetic and activation energies which would increase the probability of a reaction and therefore the reaction rate. The equilibrium constant was affected as observed by its decrease with increasing temperature. Heating time for equilibrium was also decreased with increasing temperature. The advantage of increasing the heating time was the resulting increased precipitation reaction which decreased after equilibrium due to the reverse reaction. Optimal temperature and heating time combination was determined to be 75°C for 17 hours.

CHAPTER FIVE: PERFORMANCE OF RCA WITH TYPE I UNDERDRAIN GRADATION

Objective

The ACP study found that the ideal combination of heating temperature and time was 75°C for 17 hours. This method will be used to compare the calcium carbonate yield for a limestone sample that is traditionally used for aggregate in applications like concrete and drains, with three recycled concrete (RC) samples.

Material Characterization

XRD was used to characterize the RCA samples before testing. XRD is a characterization method that can be used to determine the unit cell structure of the test material. Calcite, for example, is one polymorph of calcium carbonate. The other polymorphs have different unit cell structures and resulting XRD patterns. Figure 25 shows the rhombohedral unit cell of calcite, and the orthorhombic unit cell of aragonite, and their differing XRD patterns.

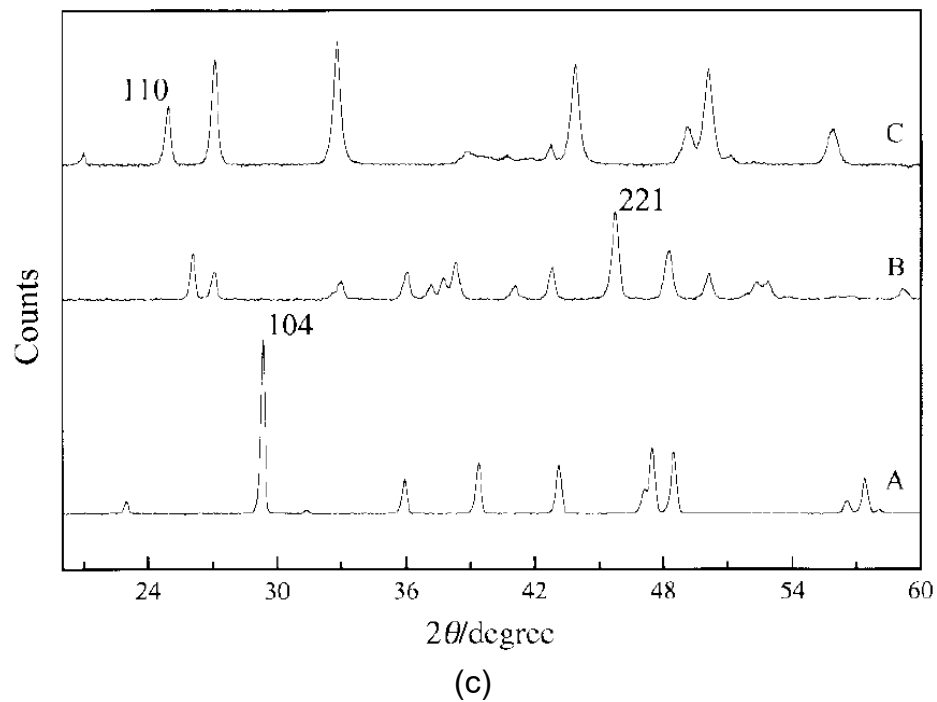
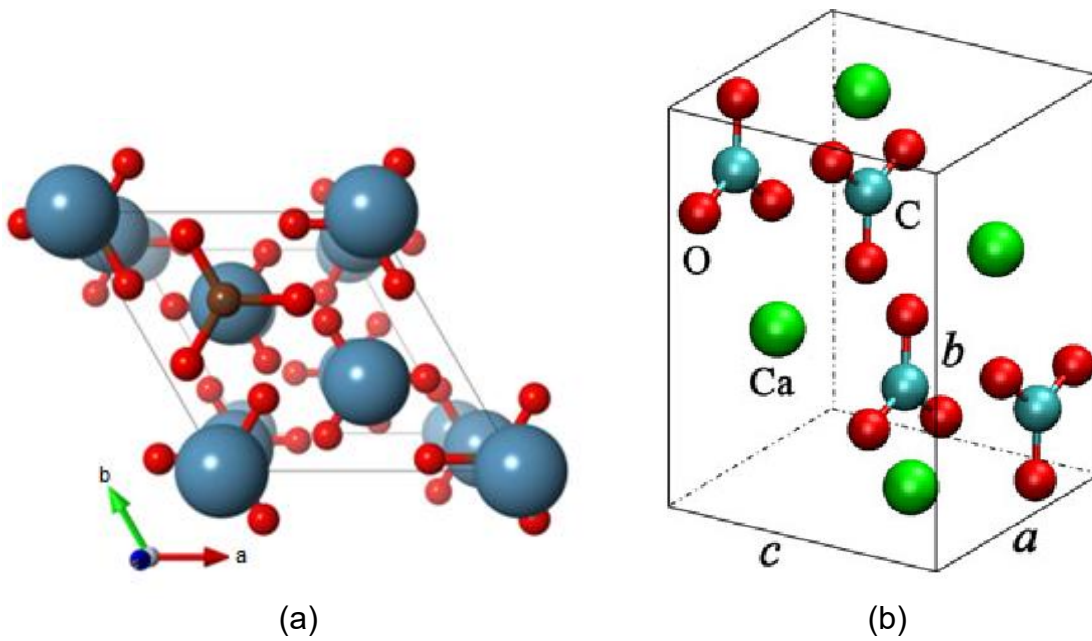


Figure 25: (a) Calcite unit cell, (b) Aragonite unit cell, and (c) XRD pattern for calcium carbonate polymorphs where A is calcite, B is aragonite and C is vaterite (Kontoyannis & Vagenas, 2000)

The XRD pattern for calcite has different peaks from the XRD pattern for aragonite. The third XRD pattern in Figure 25 is that of vaterite, whose structure is more complex than calcite and aragonite.

The first RC sample originated in a C&D waste recycling facility in Orlando, FL. It was in an outdoor environment which indicates exposure to the elements. As a result, this sample will be referred to as “weathered concrete” throughout the chapter. RC from this source was previously used for the long-term ACP test with No. 4 sized RC. XRD data for weathered concrete (Figure 26) showed the presence of quartz (SiO_2) and calcite (CaCO_3) with the dominant peak labelled for each constituent.

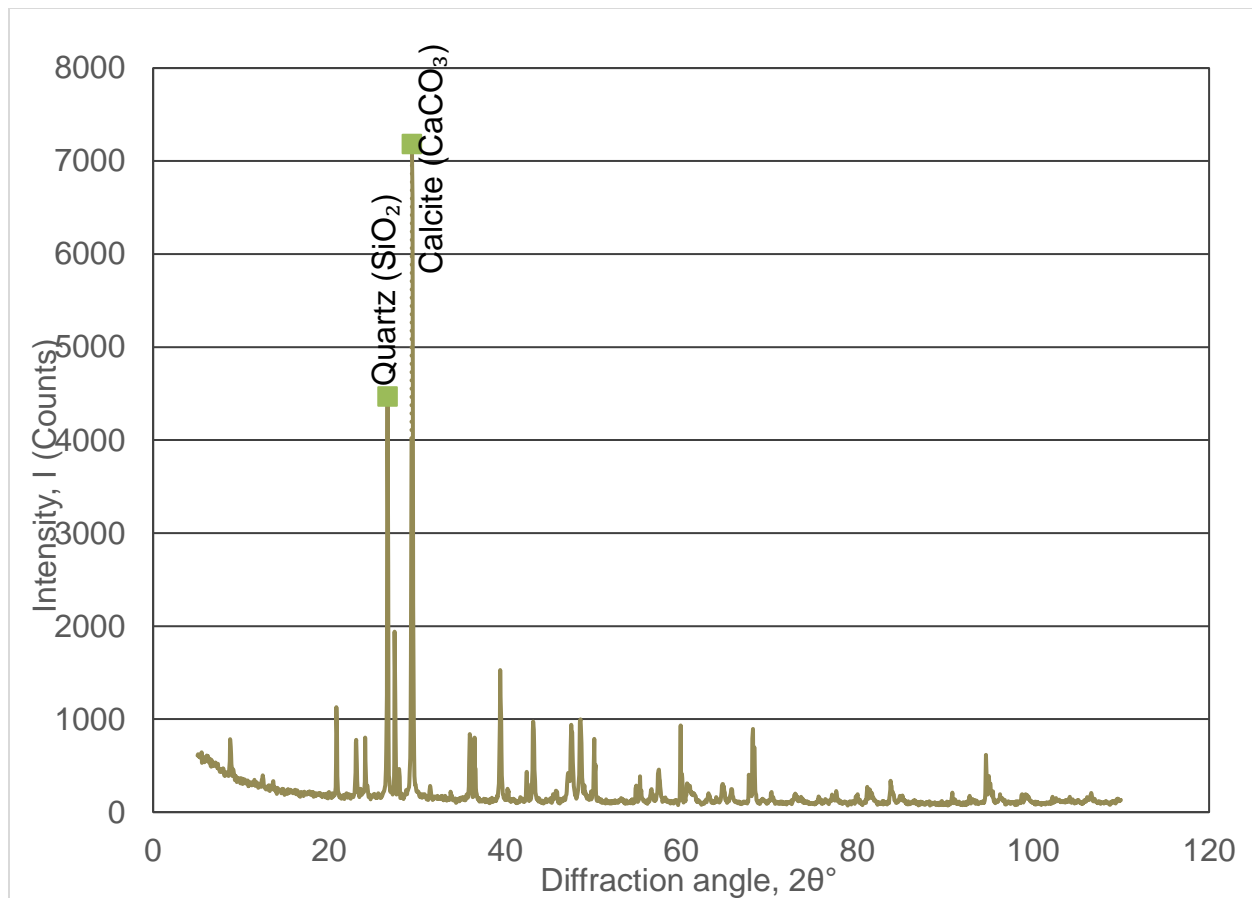


Figure 26 : XRD data showing composition of weathered concrete

The second RC sample originated from Garage C at the University of Central Florida (UCF) in Orlando, FL. This concrete sample was saved from the landfill when Garage C was being prepared for expansion in 2015. Garage C was constructed in 2000, which means that this sample was in service for 15 years before its demolition. The sample may have also been exposed to the elements if it was obtained from an external wall. There is no information available that points to the exact location from which the sample was taken from Garage C. This sample will be referred to as “demolished concrete” throughout the chapter. The XRD data for demolished concrete (Figure 27) shows the

presence of calcite and quartz, just as the weathered concrete. Figure 27 also showed the presence of portlandite ($\text{Ca}(\text{OH})_2$) in demolished concrete. Note, the dominant peak was labelled on the graph of each constituent.

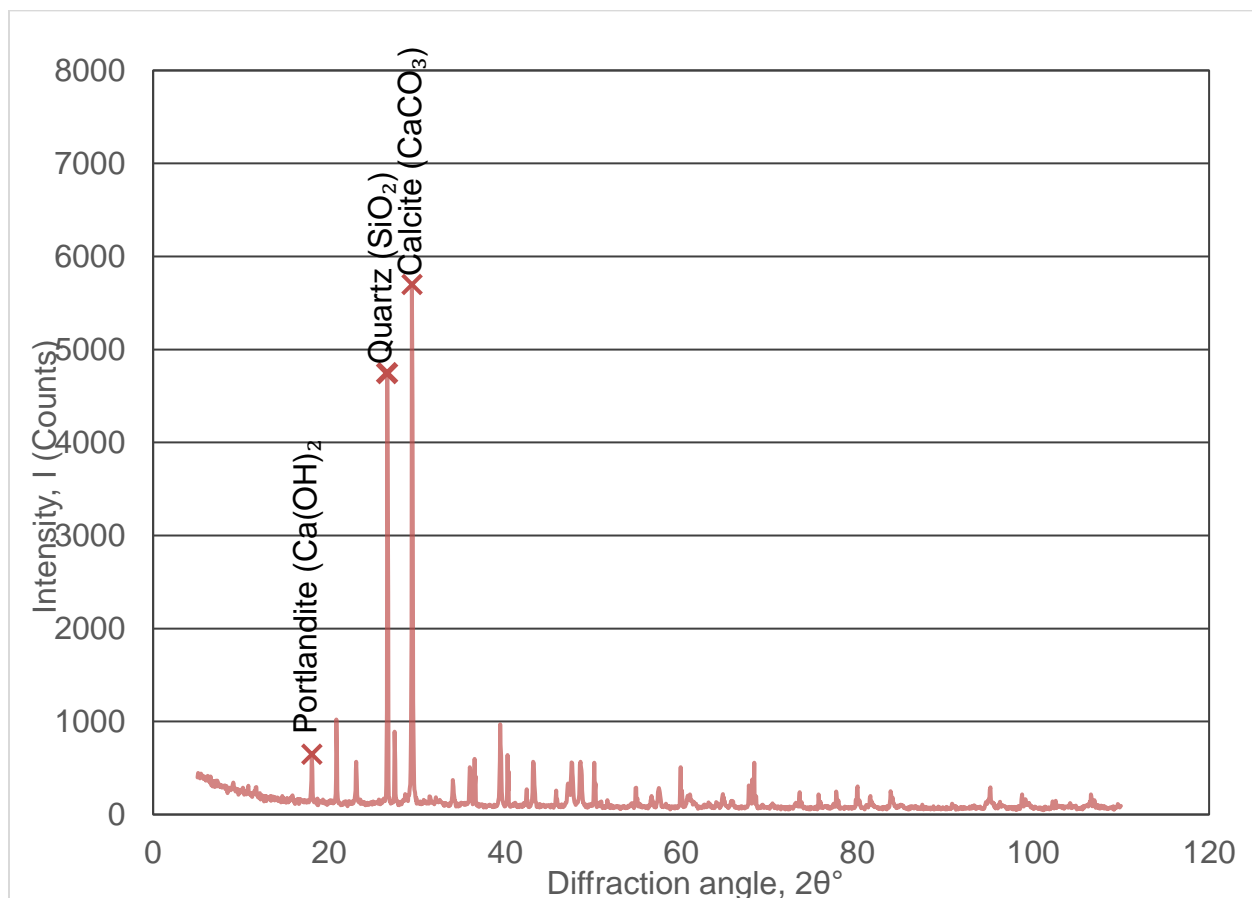


Figure 27: XRD data showing composition of demolished concrete

The third RC sample was mixed and cured for 28 days in the laboratory at UCF. This sample will be referred to as “fresh concrete” because it has not been in service. The XRD data for fresh concrete (Figure 28) shows the presence of quartz, calcite and

portlandite. Its chemical make-up is very similar to the demolished concrete. Note, the dominant peak was labelled on the graph of each constituent.

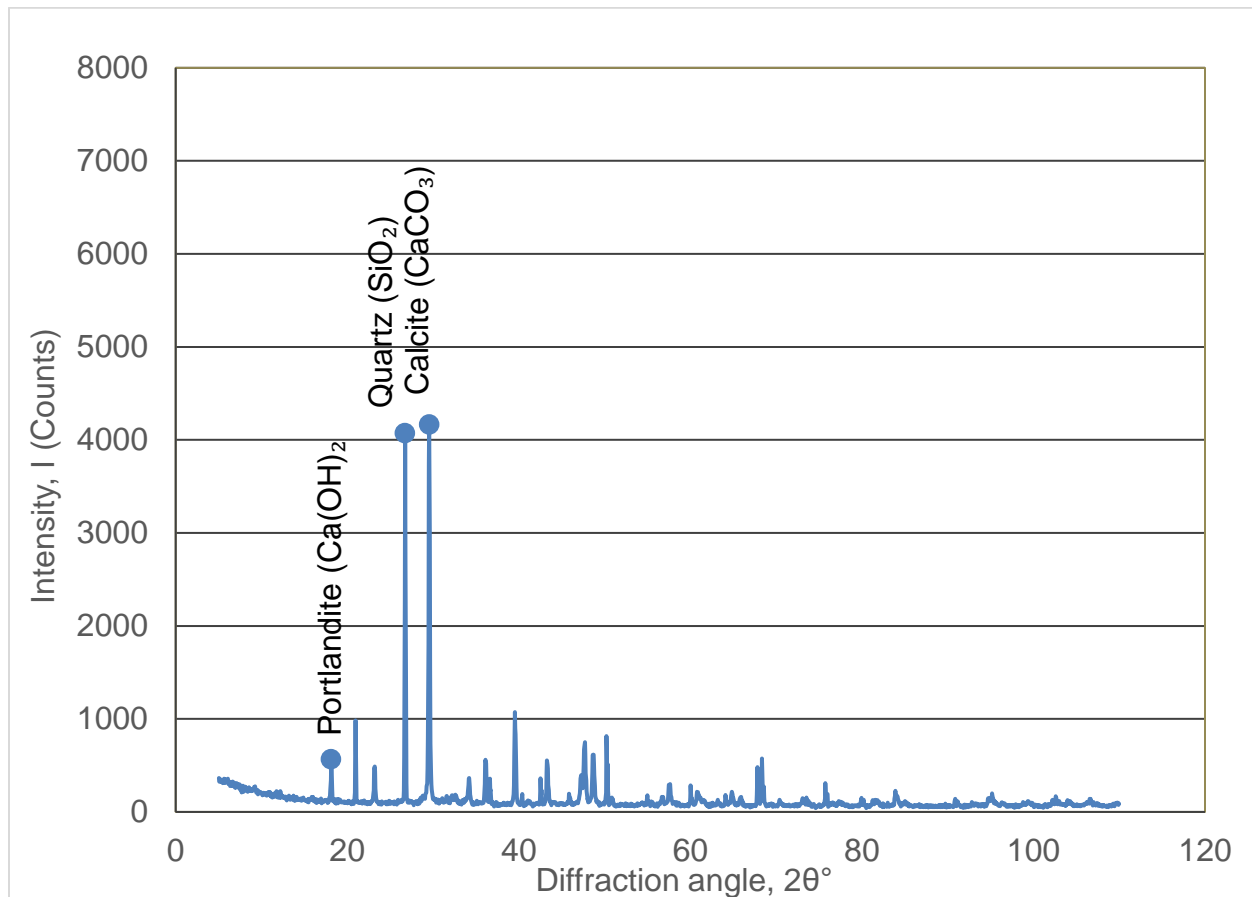


Figure 28: XRD data showing composition of fresh concrete

Figure 29 summarizes the XRD data for the RC samples. Weathered concrete has no portlandite, but the highest intensity of calcite. Demolished concrete has some portlandite and a large amount of calcite. Fresh concrete has some portlandite as well and the least calcite of all the samples. Each sample has similar counts for the quartz peak. In order to fairly compare these XRD patterns, the data was normalized by the intensity of the quartz

peak for the fresh concrete sample (Table 15). Comparison of the normalized data shows that the fresh concrete effectively had more portlandite and calcite than the demolished concrete. Weathered concrete had the most calcite. The history of portlandite suggests that it would have been exposed to the elements and experienced some carbonation.

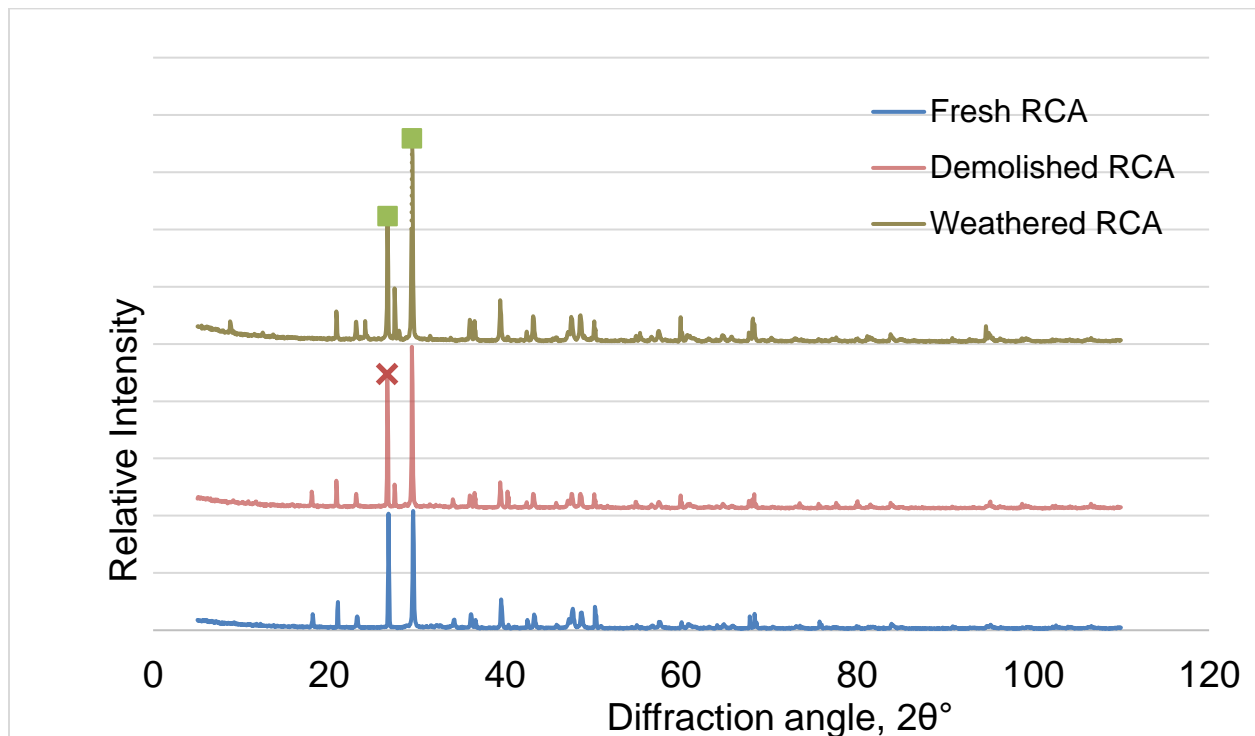


Figure 29: XRD patterns for RCA samples

Table 15: Normalized RCA data

	Intensity (Counts)					
	Raw Data			Normalized Data		
	SiO ₂	Ca(OH) ₂	CaCO ₃	SiO ₂	Ca(OH) ₂	CaCO ₃
Fresh RCA	4072	567	4164	4072	567	4164
Demolished RCA	4746	647	5700	4072	555	3572
Weathered RCA	4466		7182	4072		6548

All four of these samples were tested using the ACP method over several cycles. This objective of this experiment was to investigate the relationship between the calcium carbonate precipitation, the chemical components and the history of the RC.

Method of Investigation

Gradation

Underdrains collect and redirect subsurface water such as groundwater so that it does not saturate road subbase. Figure 30 shows Type I, II and III underdrains. FDOT design standards also specify a Type V underdrain which is more complex. Type I underdrain was chosen for this study because it is the only design to have only fine aggregate. FDOT specifications for coarse aggregate currently include the use of RCA for underdrain applications.

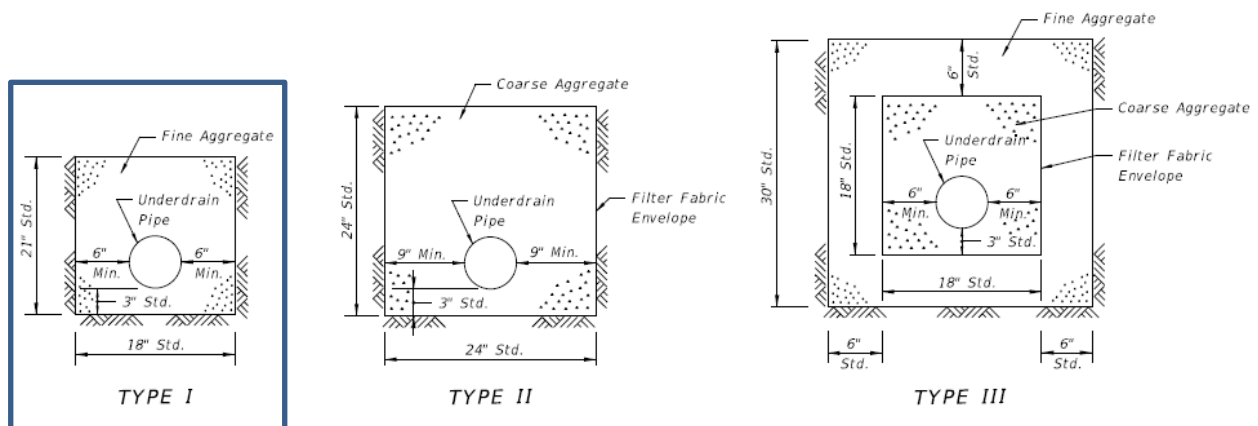


Figure 30: Underdrains

All four samples were ground and graded to meet the specifications for Type I underdrains which uses only fine aggregate (Florida Department of Transportation, 2012). Typically,

aggregate blending is used to obtain a target gradation for aggregates (Mamlouk & Zaniewski, 2010). The limitation to aggregate blending is that the materials that are blended have different initial gradation, which usually indicates that they are from different sources. In this case, each sample needed to be graded while retaining the initial chemistry and history so aggregate blending was not an ideal method. The following method was used to grade each sample.

Stockpiles were created by sieving 500 – 550 g of material. The mass retained on each sieve was then placed in secondary containment (e.g. moisture cans). The total target mass was calculated based on the limiting stockpile. The mass for each grain size was calculated. The target mass of the material for each sieve was then weighed to obtain the target gradation. The newly graded material was placed in a container and mixed to obtain uniformity.

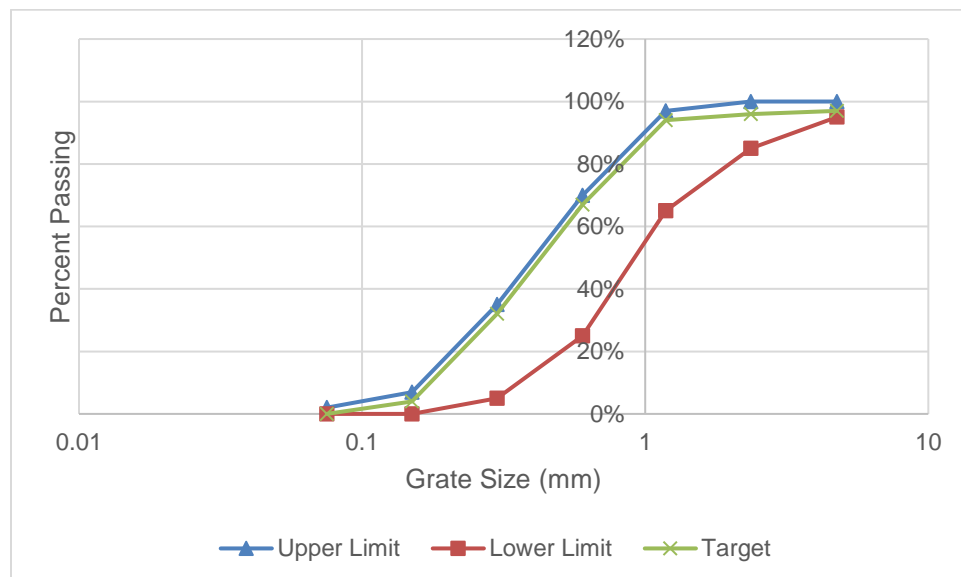


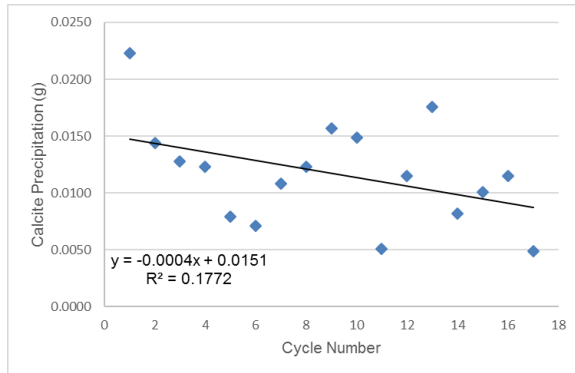
Figure 31: Gradation for Type I underdrains

ACP Test Method

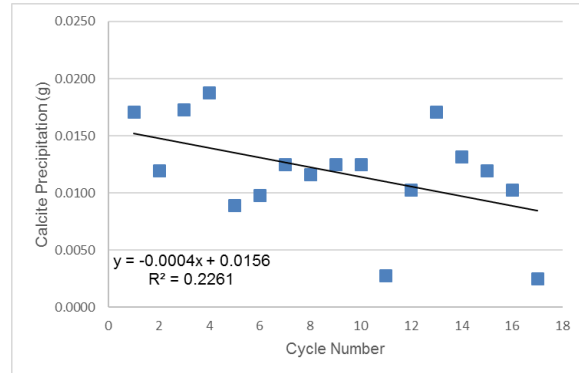
For each sample, 50 g of RCA was submerged in 100 g of water. CO₂ was injected into the solution for 5 minutes. The liquid was filtered from the solid and the leachate was placed in the furnace at 75°C for 17 hours. The solution was then filtered, and the precipitate was weighed for each sample. The results are shown in Figure 32.

Results and Discussion

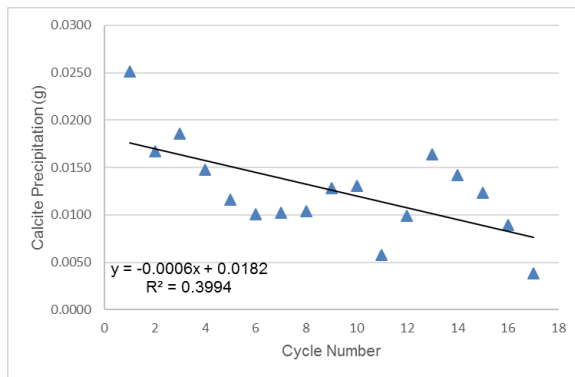
The general trends for the ACP experiments that were done on these samples are the same as the trends for the sample with No. 4 gradation (Chapter Three). Figure 32 shows the weight of the calcite precipitation for each cycle. All 4 samples followed a decreasing trend with increasing cycle number.



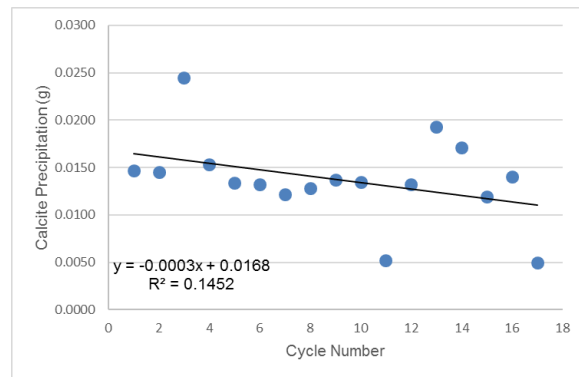
a



b



c



d

Figure 32: Resulting weight from calcite precipitation of (a) weathered RCA, (b) demolished RCA, (c) fresh RCA and (d) limestone

Figure 33 shows the cumulative calcite precipitation plotted against the cycle number. The trend for all 4 samples was polynomial due to the decreasing trend with increasing cycle number. The decreasing trend indicates that the cumulative calcite precipitation will eventually reach steady state. As previously discussed, the ACP test method is designed to simulate the chemistry that occurs in the natural subsurface environment. When subsurface drainage material (RCA or limestone) is exposed to rainwater, carbon dioxide in the rainwater forms carbonic acid to dissolve calcium ions from the material. Heating

of the leachate, which contains calcium, hydroxide, hydrogen ions, and carbon dioxide gas, is intended to accelerate the calcite precipitation reaction (page 52).

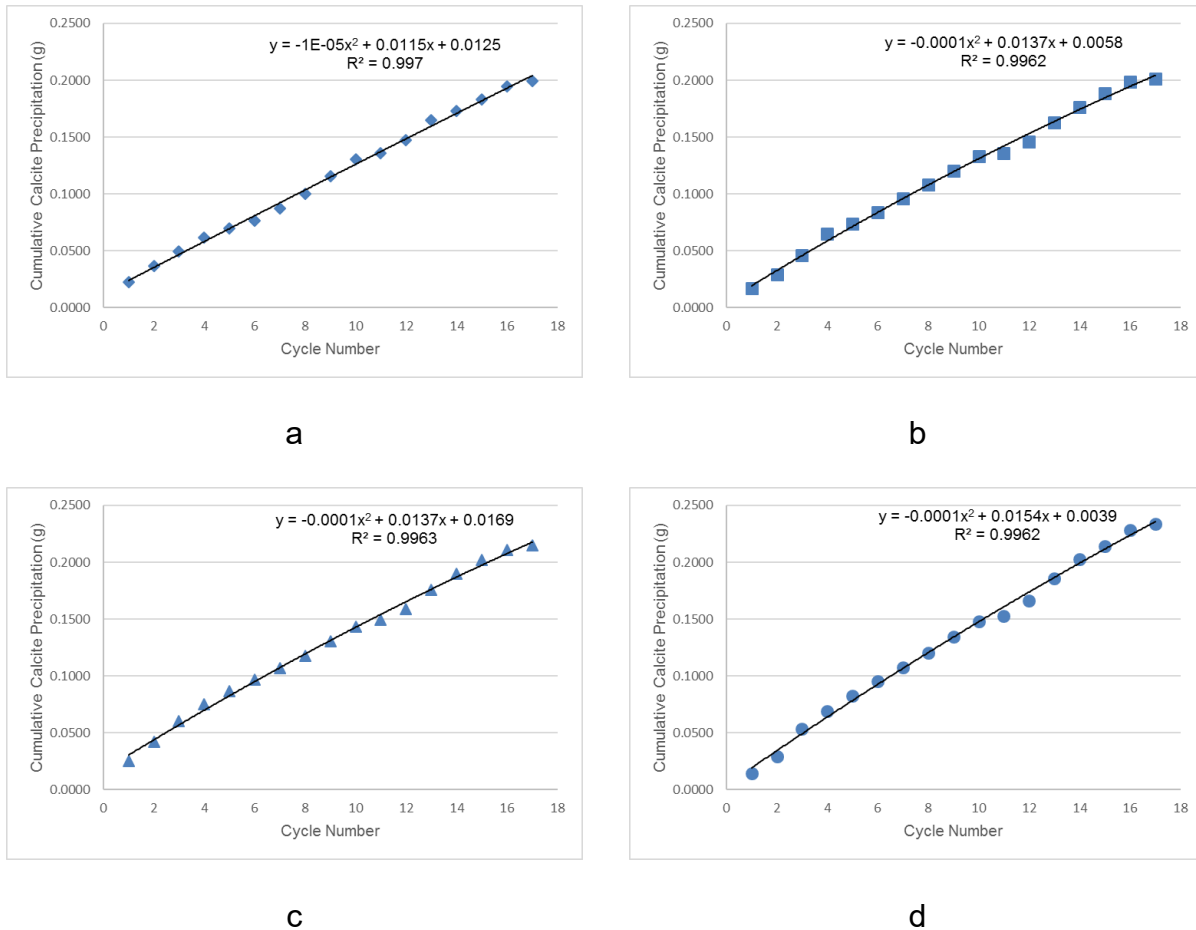


Figure 33: Cumulative calcite precipitation for (a) weathered RCA, (b) demolished RCA, (c) fresh RCA and (d) limestone

The total amount of calcite precipitated from the 50 g samples after 17 cycles is shown in Table 16 and Figure 34. The limestone sample precipitated the most calcite, whereas the weathered RCA sample precipitated the least calcite. The demolished RCA sample precipitated less than 0.01 g more calcite than the weathered RCA. The fresh RCA sample precipitated over 0.10 g more calcite than the weathered and demolished RCA

samples. High calcium limestones have at least 95% calcite. Even dolomitic limestones have at least 50% calcite. Commercial limestones typically contain less than 10% impurities. RCA contained 45% – 60% calcite which is less than most limestones. The limestone sample had more calcium ions in solution for the reaction, which explains why the limestone had the highest precipitate for 70% of the cycles and produced the most precipitate from all the samples.

Table 16: Total calcite precipitation

Sample	Total Calcite Precipitation (g)	Precipitated Calcite (%)
Weathered	0.1994	0.3988
Demolished	0.2012	0.4024
Fresh	0.2147	0.4294
Limestone	0.2335	0.4670

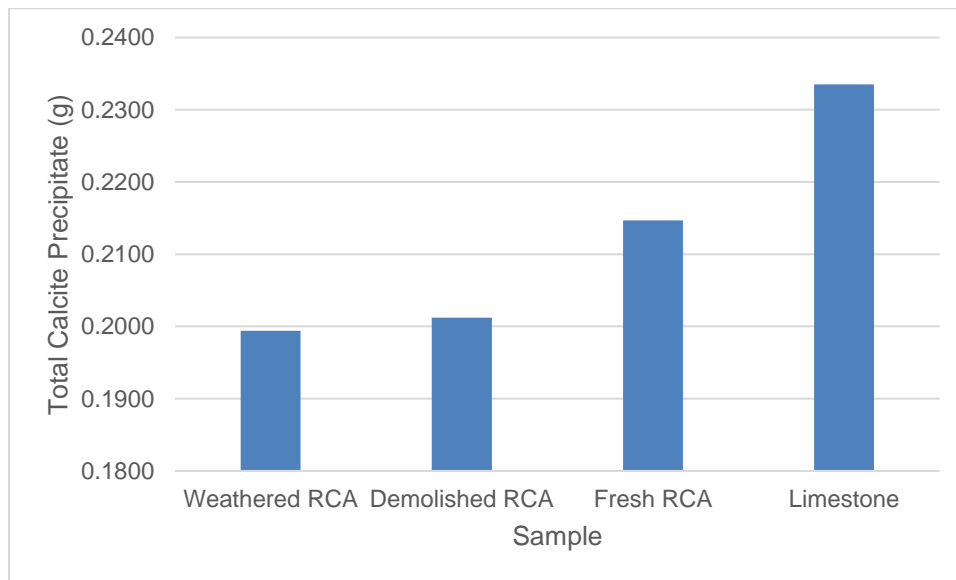


Figure 34: Total calcite precipitation

Within the RCA samples, the fresh RCA sample produced the highest mass of precipitate while the weathered RCA sample produced the lowest (Table 16 and Figure 34). One

reason is the lack of portlandite in the weathered RCA sample. Portlandite is more soluble than calcite so the portlandite in the demolished and fresh RCA samples would have more readily dissolved than the calcite in the weathered RCA sample. Recall Table 15, the normalized XRD data. The fresh sample recorded the highest intensity for portlandite, which is more soluble than calcite. The demolished sample recorded less calcite but more portlandite than the weathered sample. Portlandite is a more readily available calcium ion donor than calcite which indicates that more calcium ions were dissolved during the bubbling process for the fresh and demolished samples than the weathered RCA sample. The fresh sample with the highest portlandite content had the highest calcite precipitation yield from the RCA samples. The calcite precipitation trend follows the recorded portlandite trend, where the weathered sample with no portlandite produced the lowest total calcite precipitation. Calcite precipitation in the RCA samples are limited by the portlandite content due to its solubility.

Conclusion

The optimized ACP procedure was used to test 3 RCA samples and 1 limestone sample with differing chemistry. The RCA samples were characterized by XRD which showed various portlandite and calcite content. The samples were graded to meet Type I underdrain specifications before testing. The results showed that limestone produced the highest calcite precipitation yield due to its natural high calcite content. Within the RCA samples, the fresh concrete produced the highest yield. The portlandite content in the RCA samples had a direct correlation to the calcite precipitation yield.

CHAPTER SIX: DISCUSSION

Comparison of Results from RCA Graded for French Drain and Type I Underdrain

Applications

The study on the long-term performance of RCA for French drains yielded some positive results. The 5 kg RCA sample only produced 8 g of calcite which is 0.16% precipitated calcite in 36 cycles. The study also found that RCA yielded twice as much calcite precipitation as limestone. That study was specific to the French drain system. A more general approach to calcite precipitation was investigated by varying the experimental parameters of the ACP method, namely the heating time and temperature. In this study, the surface area was increased to maximize the calcite precipitation. The enhanced ACP method was determined to have a longer heating time and lower temperature than the original procedure as seen in Table 17.

Table 17: Comparison of the ACP method for weathered RCA sample

	Original ACP Method	Enhanced ACP Method
Gradation (FDOT Standard)	No. 4	Fine Aggregate
Surface Area	Low	High
Heating Temperature	110°C	75°C
Heating Time	4 hours	17 hours
No. of Cycles	36	17
Precipitated Calcite	0.16%	0.3988%

The results for the weathered RCA sample were also shown in Table 17. The weathered RCA sample was used for comparison because the same source material was used in both ACP experiments. The enhanced ACP procedure, with the lower temperature, longer

heating time and higher surface area resulted in more than double the precipitated calcite. As discussed in Chapter Four, increased heating time and a moderate increase in temperature work together to produce a higher yield of calcite precipitation. The increased precipitation is also attributed to the increased surface area which agrees with the discussions of increasing calcite precipitation with increased fines in Chapter Three.

The results of calcite precipitation in limestone is also worthy of comparison. In the original ACP method, RCA produced twice as much calcite precipitation as limestone whereas limestone produce more calcite precipitation with the enhanced ACP method (Table 18). There are a few factors that can be considered with this comparison.

Table 18: Comparison of calcite precipitation from limestone

	Original ACP Method	Enhanced ACP Method
RCA	1.4579 g	0.1994 g
Limestone	0.7441 g	0.2335 g

The limestone used in both methods may have had different calcite concentrations. If the limestone that was used in the original ACP method was magnesian or dolomitic and the one in the enhanced ACP method was high calcium, then the high calcium limestone would reasonably yield more calcite precipitation than the magnesian or dolomitic limestone.

In the original ACP experiment, the limestone and RCA were in the coarse aggregate form. During the CO₂ bubbling process, the carbonic acid would need to diffuse into the

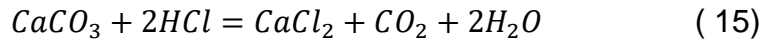
coarse aggregate to release the calcium ions into the solution. The RCA bonds would require less energy to break than that of the limestone bonds. RCA bonds have had some years to form and crystallize whereas the limestone bonds have had thousands of years.

In the enhanced ACP experiment, the limestone and RCA were tested as finer material. The surface area was much larger for the limestone in this experiment than the original ACP method. The limiting factor was most likely the initial concentration of calcite rather than the ability for the carbonic acid to diffuse into the surface of the solid rock sample. The weathered RCA sample had a limited calcite concentration compared to limestone with the potential for 95% calcite that was readily available for dissolution in the bubbling phase due to the fine gradation.

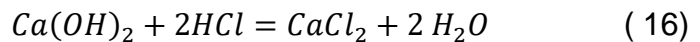
Methods for Measurement

ACP was developed to simulate subsurface environments and drainage systems where calcite-containing aggregate such as RCA can be dissolved to produce calcium-rich waters and precipitate calcite when exposed to the atmosphere. Geotextiles in subsurface drains risk clogging when exposed to calcite precipitate. The goal of the ACP method is to measure clogging potential. Calcium in the form of calcite is measured by dissolving the calcium ions from the sample, then heating to accelerate precipitation. Calcite precipitate is weighed after being filtered from solution. Other methods can be used to measure calcite.

Acid washing is a method that is based on the selective exothermic reaction shown in equation 16.



Calcium-rich samples such as limestone would completely react with hydrochloric acid (HCl) to form calcium chloride and carbon dioxide. Calcium would no longer be bonded to the sample in carbonate form. The difference in sample weight before and after the reaction would be due to the calcite loss, which directly relates to calcium ion content. Heterogeneous samples such as RCA has calcium-containing calcite and portlandite, as well as non-calcium containing quartz. The calcite would react with HCl as previously discussed with limestone and portlandite reacts with HCl according to equation 16.



Quartz is not as reactive as calcite when exposed to HCl. Acid washing of RCA, then, would leave quartz after the calcite and portlandite reactions are complete. Again, difference in weight of the sample before and after acid washing would indicate calcium content.

Acid digestion is another method for measuring calcium content. In this method, acid is added to the sample which is then heated until complete decomposition occurs. Material characterization methods such as spectrometry can be applied to the decomposed sample to determine metal content. Palma et al used atomic absorption spectrophotometry to evaluate ion concentrations from animal carcass, bone, excreta, concentrate, forage and feces samples (Palma, et al., 2015). Guo et al, Wracker et al and

Muller et al used phosphoric acid digestion to analyze oxygen and carbon isotopes of carbonate materials. The carbon dioxide that was released during acid digestion of sample was trapped and compared to an isotopologue of a sample CO₂ gas (Guo, et al., 2009; Muller, et al., 2017; Wacker, et al., 2016). Both applications of acid digestion relied on full decomposition of the sample and subsequent measurement to determine the required mineral/gas concentration.

If applied to the study of calcite precipitation for drainage applications, acid washing and acid digestion methods would measure all of the calcium in a sample. Such a measurement would be comparable to results from the long term ACP method which aims to measure the calcite precipitation of a sample throughout its life. Long term ACP depends on calcium dissolution in a weak acid (carbonic acid) and concludes when no calcite precipitation is produced (Table 9). It follows that the sample or solution may have calcium ions even when no calcite precipitation is produced. For the purposes of the ACP method, it is acceptable to still have calcium ions in the sample or solution at the end of the experiment because the method was developed to measure the calcite precipitation potential in drainage applications where the aggregate would be exposed to carbonic acid. The point is that measurement from acid washing and acid digestion techniques would consider calcium ion content, not necessarily the reaction potential for drainage applications.

Study Limitations

The following limitations have been recognized in this study.

- Long term ACP method was designed to capture the total calcite precipitate over the “lifetime” of the sample. In Chapter Three, the calcite precipitate yield at the end of cycle 28 was one order of magnitude less than the calcite precipitate yield from the first cycle. The significant decrease in calcite precipitate yield indicated the approach of the end of the experiment. The correlation value for the plot with all 30 cycles was $R^2 = 0.643$. The samples in Chapter Five did not show as significant a decrease in the 17 cycles that were recorded for those samples. These results cannot truly be considered “long-term” or “lifetime” calcite precipitation for the samples. Seventeen cycles for the type I underdrain samples is approximately half the number of cycles for the No. 4 graded RCA sample. The number of cycles of the long-term test do not provide enough data for as high a correlation as the No. 4 RCA sample with 30 cycles.
- The RCA samples were characterized with XRD before the ACP test was performed. The limestone was not characterized. The resulting precipitate was not characterized either. Characterization of the limestone would be helpful to compare with the chemistry of the RCA samples. Precipitate characterization would not only confirm that calcium carbonate was the product but would also provide insight to the specific polymorph of calcium carbonate that was created.
- There are a couple notable limitations within the ACP procedure. Calcite precipitation measurements were accomplished by measuring the suspended solids in the solution rather than the dissolved solids. The total dissolved solids may be a significant measurement of calcite that has nucleated but has not formed

a crystal that is large enough to be filtered. Another procedural consideration is the use of tap water instead of distilled water. Tap water contains chemicals from treatment in the distribution system which may interact with the ions and molecules in the solution. The effect of the chemicals in the tap water should be investigated to determine its significance.

CHAPTER SEVEN: SUMMARY AND CONCLUSIONS

Summary

Studies have shown that the fines content and calcite precipitation have been factors in the clogging of geotextiles when RCA is used in subsurface drainage systems. This study investigated the clogging potential of RCA in French drain and Type I Underdrain applications.

For French drain applications, the short term and long-term prototype ACP procedures were used to test calcite precipitation potential of RCA and compare it to natural aggregate such as limestone. From the short-term procedure, calcite precipitation production from RCA was double that of limestone. The long-term ACP procedure simulated and accelerated the natural calcite precipitation process which yielded the “life-time” calcite precipitate for the RCA sample.

The ACP experiment was investigated by varying heating time and heating temperature to optimize the reaction rate for each cycle. Samples had a higher surface area than in the prototype ACP experiment. The resulting optimized ACP experiment had an increased calcite precipitation yield.

The optimized ACP experiment was used to compare the calcite precipitation for 3 RCA samples and 1 limestone sample. RCA samples in this investigation initially had varying times of field service that affected their portlandite content. Time in service is directly

related to the carbonation of portlandite to calcite in the RCA samples. The limestone sample was assumed to be a high calcium limestone. All samples were graded to meet the FDOT specifications for Type I Underdrains.

Results for the weathered RCA sample was used to compare the prototype and optimized ACP methods. The prototype ACP method used No. 4 gradation with a 4 hour heating time and 110°C heating temperature while the optimized ACP method used Type I Underdrain gradation with a 17 hour heating time and 75°C heating temperature. Both experiments followed the long term procedure for which the prototype ACP method had 30 cycles and the optimized ACP method had 17 cycles.

Conclusions

Conclusions on the clogging potential of RCA with No. 4 gradation for French drain applications.

- The comparison of calcite precipitation of RCA and limestone showed that RCA produced twice as much calcite as limestone. Further investigation with different gradation (Chapter 5) demonstrated that the soluble portlandite in RCA is a factor in these results.
- When RCA fines content was varied, the results showed that the increase in fines produced higher calcite precipitation yield. These results, along with previous permeability study on the clogging potential show that RCA fines contribute to

physical and chemical clogging of geotextile filter fabric.

- 8 g of calcite was precipitated from a 5000 g RCA sample under the worst environment. Carbon dioxide injection ensured that the sample was exposed to a higher concentration than atmospheric carbon dioxide, thereby creating an unnaturally acidic environment. Even with the acidic environment, the RCA sample produced 0.16% calcite. Thus, calcite precipitation may have a negligible effect on clogging.

Conclusions from the investigation of the ACP procedure.

- Increasing temperature and reaction time contributes to an increase in calcite precipitation yield by increasing kinetic and activation energy for the reaction to occur. The yield increase was limited by the potential for dissolution of the precipitate after the reaction reaches equilibrium. The optimum heating time and temperature combination from conducted experiments was 17 hours at 75°C.

Conclusions from the performance of RCA and limestone with Type I Underdrain gradation.

- Portlandite observed in the fresh and demolished RCA caused higher calcite precipitation than the weathered RCA due to the difference in solubility of calcite and portlandite. Less portlandite was observed in samples with exposure to the elements which was likely due to carbonation.

- Calcite precipitation potential for RCA in Type I Underdrains was observed to be less significant than the precipitation of limestone in the conducted experiments. In this case, the samples were graded to have a higher surface area than the short term ACP test. As a result, the solubility of portlandite in RCA did not have as much of a significant effect in this test.

Overall, this study concludes that RCA suitability for drainage applications depends on its chemistry, specifically portlandite and calcite content, as well as its gradation.

Recommendations

The following are recommendations for study to further optimize the ACP method and maximize its applications.

Investigate the significance of TDS in the solution

The measurement of total suspended solids provides a good starting point for quantitative determination of calcite precipitation in the ACP procedure. The nucleation and growth of calcite crystals in solution may also be a significant contribution to the measured precipitate.

Investigate the significance of surface area

Surface area was increased significantly between the prototype ACP method and the optimized ACP method. The latter produced a higher yield of calcite precipitation with the increased heating time and lower temperature.

Numerical Analysis of the ACP Procedure

Numerical simulation can be used to investigate the effects of each variable and further optimize the ACP procedure. This study investigated three temperatures and nine heating times with one RCA sample to optimize the procedure and then tested the new procedure on three RCA samples. Numerical simulation with multi-variable analysis provides the capability to increase the range of variables tested and identify correlation between them.

Use of ACP procedure as pre-treatment for RCA

Aggregate washing is a treatment process that is used to remove fines from aggregate to reduce the risk of poor drainage performance. Equipment such as log washers, barrel washers, vibrating wet screens and coarse aggregate scrubbers are used by aggregate washing plants (Figure 35). These machines may use a combination of suspension, abrasion and pressurized washing to separate fines from the coarse aggregates. The removal of loose debris, for example, may be accomplished with pressurized water while adhered fines, such as fines on concrete, may require abrasion techniques for removal (Dull, 1914). This study has employed the ACP procedure as an evaluation method for the calcite precipitation potential of RCA. Results of the prototype and optimized ACP methods demonstrate the potential for the calcite to be removed from RCA to obtain acceptable concentrations. Pre-removal of calcite would significantly reduce the risk of calcite precipitation for RCA that replaces aggregate in drains.



a



b

Figure 35: Aggregate washing equipment (a) log washer and (b) coarse aggregate washer

APPENDIX A
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**Title:** Long-Term Performance of
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Subsurface Drainage**Author:** Toni McCulloch, Donghoon Kang,
Ryan Shamet, et al**Publication:** Journal of Performance of
Constructed Facilities**Publisher:** American Society of Civil
Engineers**Date:** 02/13/2017

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APPENDIX B
DIGI-WEIGH B2004 SPECIFICATIONS

model	DWP-B2004
max metage	200g
Min metage	0.0001g
reproducibilit y	± 0.000 1g
Linearity error	± 0.0003 g
Steady time	≤ 8 s
Work temperature	17.5℃-22.5℃
Size of balance pan	$\Phi 80$ mm
Size of windproof cover	225mm \times 220mm \times 265mm
Dimension	340mm \times 215mm \times 350mm
weight	7.2kg
Power supply	AC adapter

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